Journal of the Institute of Petroleum

VOL. 41 NOVEMBER 1955 No. 383

CONTENTS

Determination of Magneto-optical Rotation of Hydrocarbons in the Ultra-violet Region
By F. H. Garner, O.B.E., C. W. Nutt, and A. Labbauf

Polymerization of Propene with a Silicotungstic Acid Catalyst
By J. J. Verstappen and H. I. Waterman

Abstracts 1389–1509

Book Reviews

Additions to Library

PRICE 10s 0D A COPY OR £4-14-6 YEARLY *POST FREE*

Published by the Institute of Petroleum 26 Portland Place London W1

Printed in Great Britain by Richard Clay and Company Ltd Bungay Suffolk

COUNCIL, 1955–56

President

Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.

Past-Presidents

T. Dewhurst, A.R.C.S.
A. E. Dunstan, D.Sc., F.R.I.C.
E. A. Evans, M.I.Mech.E., F.R.I.C.
F. H. Garner, O.B.E., Ph.D., F.R.I.C.
H. S. Gibson, C.B.E., M.A., M.I.Mech.E.
C. A. P. Southwell, C.B.E., M.C., B.Sc.

Vice-Presidents

E. B. Evans, M.Sc., Ph.D., F.R.I.C.
A. C. Hartley, C.B.E., F.C.G.I., B.Sc.(Eng.), M.I.C.E., M.I.Mech.E.
F. Morton, Ph.D., D.Sc., F.R.I.C.
J. A. Oriel, C.B.E., M.C., M.A., B.Sc., F.R.I.C., M.I.Chem.E.
E. J. Sturgess, B.Sc.
G. H. Thornley, M.Sc.

Members of Council

W. S. Ault, B.A.
V. Biske, B.Sc., LL.M., F.R.I.C.
C. D. Brewer, M.I.Mech.E.
E. J. Dunstan, M.Sc., M.I.Chem.E.
F. L. Garton, M.A., B.Sc.
A. J. Goodfellow, B.Sc., A.R.I.C.
N. W. Grey, M.I.Chem.E., M.E.I.C.
E. LeQ. Herbert, B.Sc., F.R.I.C., M.I.Chem.E.
H. Hyams
E. C. Masterson, B.Sc.
T. W. Mathias, O.B.E., M.A.
J. S. Parker, M. A., B.Sc.
A. J. Ruthven-Murray, C.M.G., M.A., B.Sc.
D. L. Samuel, B.Sc., A.R.I.C.
G. H. Smith, Ph.D.
R. B. Southall, C.B.E.
A. R. Stark, B.Sc., A.R.I.C.
W. H. Thomas, A.R.S.M., F.R.I.C.
O. F. Thompson, O.B.E.
A. T. Wilford, B.Sc., F.R.I.C.
C. G. Williams, D.Sc., M.I.Mech.E., F.R.Ae.S.
C. S. Windebank, B.Sc., M.S.

Ex-Officio

S. A. Berridge, B.Sc. Fawley Branch
W. H. Davies. London Branch
G. M. Davies. Northern Branch
W. M. Stirling, A.H-W.C., A.M.I.E.E. Scottish Branch
J. R. Moore. South-Eastern Branch
A. S. Brooman, B.Sc. Stanlow Branch

Honorary Secretary

C. Chilvers, B.Sc., F.R.I.C.

Honorary Treasurer

G. H. Coxon

General Secretary

D. A. Hough, T.D., F.I.A.C.

Honorary Editor

E. B. Evans, M.Sc., Ph.D., F.R.I.C.

Honorary Associate Editor

D. L. Samuel, B.Sc., A.R.I.C.

Editor

George Sell

Honorary Secretaries of Branches

Bahrein Branch: R. B. Bennett, c/o Bahrein Petroleum Co. Ltd., Awali, Bahrein, Persian Gulf.

Fawley Branch: S. A. Berridge, B.Sc., c/o Esso Petroleum Co. Ltd., Fawley, Southampton.

Kuwait Branch: J. G. Cooper, c/o Kuwait Oil Co. Ltd., Ahmadi, Kuwait, Persian Gulf.

London Branch: R. F. Leach, M.A., c/o Shell-Mex and B.P. Ltd., Shell-Mex House, Strand, London, W.C.2.

Northern Branch: H. Kaye, B.Sc., A.M.I.Chem.E., c/o Manchester Oil Refinery Ltd., Twining Road, Trafford Park, Manchester 17.

Scottish Branch: W. M. Stirling, A.H-W.C., A.M.I.E.E., Scottish Oils Ltd., Middleton Hall, Uphall, Broxburn, W. Lothian.

South-Eastern Branch: J. R. Moore, Fisher Governor Co. Ltd., Airport Works, Rochester, Kent.

South Wales Branch: D. J. Lewis, National Oil Refineries Ltd., Llandarcy, Glam.

Stanlow Branch: A. S. Brooman, B.Sc., 11 Granse Crescent, Hooton, Wirral, Cheshire.

Trinidad Branch: J. L. Deal, B.Sc., Trinidad Leaseholds Ltd., Pointe-à-Pierre, Trinidad, B.W.I.

DETERMINATION OF MAGNETO-OPTICAL ROTATION OF HYDROCARBONS IN THE ULTRA-VIOLET REGION*

PART I. ANOMALOUS DISPERSION IN THE REGION OF ABSORPTION

By F. H. GARNER, O.B.E., C. W. NUTT, and A. LABBAUF

SUMMARY

A method has been developed for the measurement of the magneto-optical rotation of a few drops of liquid in a micro-polarimeter cell designed for this purpose. In this way, the rotation of solutions of several moderately absorbing organic compounds has been measured in the ultra-violet region. The solutes investigated included benzene, anthracene, *cyclo*hexanone, 1,2,4-trichlorobenzene, and camphor.

The results obtained, although on two-component systems, show the existence of anomalous magneto-optical rotation through the absorption band, and are discussed in relation to the theories of magneto-optical rotation. Of the compounds investigated the first four gave results consistent with the theory for diamagnetic materials, whilst camphor showed results similar to that predicted for a paramagnetic substance.

INTRODUCTION

MAGNETO-OPTICAL phenomena are generally divided into two classes, the Zeeman effect and the Faraday effect.[1] The former is a change in frequency, accompanied by polarization of light when the emitter is subjected to a magnetic field, and the latter is rotation of the plane of polarization of plane polarized light when it is passed through a homogeneous substance, along the lines of force of a magnetic field.

A general theory to explain the Faraday effect satisfactorily has not as yet been given. The quantum mechanical theory for atoms by Rosenfeld, and for molecules by Serber, predicts the magneto-optical rotation if the energy levels, the probability of transition, and the proper quantum number for the atoms and molecules are known.

The Becquerel formula :

$$V = \frac{e}{2mc^2} \cdot \frac{dn}{d\lambda} \cdot \lambda,$$

where V = Verdet constant in radians/Gauss cm,
e = electronic charge in e.s.u.,
m = mass of electron in g,
c = velocity of light in cm/sec,
n = refractive index, and
λ = wavelength,

is a good representation of the variation of the magneto-optical rotation with wavelengths for monoatomic gases. In the case of molecules, gaseous or liquid, where Larmor's theorem [20] fails to hold, its application involves the use of a numerical factor, γ, called the optical anomaly.

$$V = \gamma(e/2mc^2)(dn/d\lambda) \cdot \lambda$$

Drude [2] has treated the subject very thoroughly and has put forward two explanations for the phenomenon. One theory is based on the hypothesis of the Hall effect and the other on the molecular currents. His final equation can be derived by starting with the usual refraction dispersion formula for gases :

$$n^2 - 1 = (4\pi e^2/m)[Nf/(\omega_0^2 - \omega^2)]$$

where ω = frequency of the light,
N = number of atoms/cm^3,
f = restoring force/cm of oscillator of characteristic frequency ω_0.

Under the magnetic field, if both Zeeman components are represented by $\omega\pm$, the densities of atoms by $N\pm$ and the oscillator strengths of $f\pm$ and if n be replaced by n_+ or n_-, it is then justifiable to write,

$$-\delta n = n_+ - n_- = \left(\frac{\partial n}{\partial \omega_0} \cdot \delta\omega_0 + \frac{\partial n}{\partial N} \cdot \delta N + \frac{\partial n}{\partial f} \cdot \delta f\right)$$

When this is combined with the formula of Becquerel it gives

$$\alpha = \frac{4\pi e^2}{nmc} \cdot \mu_0 \cdot NfL\left[A\,\frac{\omega^2}{(\omega_0^2 - \omega^2)^2} + \frac{B}{2}\,\frac{\omega^2}{\omega_0(\omega_0^2 - \omega^2)\Delta\omega_0} + \frac{C}{2}\,\frac{\omega^2}{\omega_0(\omega_0^2 - \omega^2)}\,\frac{h}{kT}\right],$$

where α = angle of rotation,
L = path length in the medium,
$\mu_0 = \dfrac{eH}{2mc}$ = Larmor's orbital frequency, and
H = magnetic field strength.

If the original dispersion formula of Drude does not meet the requirements, the Lorenz–Lorentz formula can be applied,

$$(n^2 - 1)/(n^2 + 2) = (4/3) \cdot (\pi e^2/m) \cdot [Nf/\omega_0^2 - \omega^2)]$$

The final equation will be of the following form :

$$\alpha = NHL\left[\frac{(n^2 + 2)^2}{9n}\right]\sum_K\left[A_K\,\frac{\omega^2}{(\omega_K^2 - \omega^2)^2} + B_K\,\frac{\omega^2}{(\omega_K^2 - \omega^2)} + \frac{C_K}{T}\,\frac{\omega^2}{(\omega_K^2 - \omega^2)}\right],$$

* MS received 22 March 1955.

where $\sum_K$ indicates that the summation should be taken over K characteristic frequencies. This three K-termed formula, as it is called, represents the magneto-optical rotation exactly in non-absorbing regions. The A-term represents the diamagnetic partial rotation, the sign of which remains unchanged through the absorption band. The other two terms represent rotations of opposite sign on both sides of the absorption band.

The two theories of Drude, however, lead to two inconsistent conclusions. The one based on the hypothesis of the Hall Effect indicates rotations of similar sign on both sides of the absorption line, whereas the other, based on the hypothesis of molecular currents, represents a dispersion curve with oppositely directed branches on the opposite edges of the absorption region. There is, however, experimental evidence in favour of the latter.

Dorfman [3] and Ladenburg [19] show how these opposed predictions are reconciled by a theoretical treatment based on a wave-mechanical consideration of the problem.

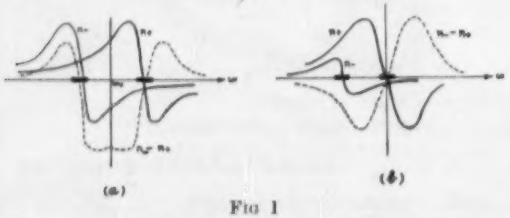
From the theoretical view-point, the problem can be treated by considering the longitudinal Zeeman effect in absorption. The effect of moderate magnetic fields on the optical properties of matter comprises three effects:

(1) The splitting of spectral lines into $\pm$ circularly polarized light.

(2) The symmetry of intensities of Zeeman components indicating Paschen–Back effect.

(3) The asymmetry of intensities of Zeeman components in paramagnetic atoms at low temperature.

Under a magnetic field the absorption line of a substance is split into a doublet, one being the + circular component and the other the − circular component.



(a) (b)

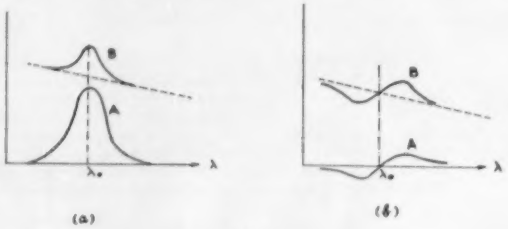
FIG 1

REFRACTION DISPERSION CURVES FOR +VE AND −VE CIRCULARLY POLARIZED COMPONENTS OF LIGHT IN: (a) DIAMAGNETIC, AND (b) PARAMAGNETIC MATERIALS

There will therefore be two dispersion curves for the magnetized medium. Diagrammatically, this has been represented in Fig 1 (*a*). It refers to the diamagnetic Faraday effect, *i.e.* where the two absorption doublets are symmetrical. The problem of the paramagnetic Faraday effect has similarly been represented in Fig 1 (*b*). Here, since the two absorption doublets are asymmetric, *i.e.* one component is absorbed more intensely than the other, the refraction dispersion curve takes the form as shown.

Fig 2 (*a*) and (*b*) are schematic representations of diamagnetic and paramagnetic Faraday effects respectively. In both diagrams, curve A represents the rotation due to the characteristic wavelength λ_0 and curve B the superimposed rotation due to other wavelengths.

Cotton, one of the original workers, has measured the magneto-optical rotation of aqueous solutions of $CrCl_2$ and $CoCl_2$ and has observed anomalous behaviour



(a) (b)

FIG 2

THEORETICAL MAGNETO-OPTICAL ROTATION DISPERSION CURVES IN: (a) DIAMAGNETIC, AND (b) PARAMAGNETIC MATERIALS

close to both sides of the absorption bands.[4] Scherer has been able to extend observations farther into the absorption region with similar results.[5] The results for $CoCl_2$ solutions support the theory of a paramagnetic Faraday effect, this behaviour being attributed to the paramagnetic nature of cobalt ions. The same authors [6] have also measured the magneto-optical rotation of thiobenzophenone and observed anomalous behaviour on both sides of the absorption band. Their rotation dispersion curve is typical of a diamagnetic Faraday effect. Wood has measured the magneto-optical dispersion of sodium in the vapour state.[7] His results show rotations of similar sign on both sides of the absorption line. Also noteworthy is the same author's work on rare-earth salt solutions.[8] Here, Wood does not put much emphasis on the accuracy of his results, but the dispersion curves are instructive in that they convey the typical form of what is expected from theory.

The theoretical difficulty in the interpretation of the results is that if there is quite a small A-term (diamagnetic term) present it would totally mask the effect of the B-term (paramagnetic term) when the wavelength of the incident light is near the absorption band. If both A- and B-terms are present, then the search for the B-term should be made at regions comparatively far from the absorption region.

APPARATUS

The apparatus consisted of the light source, the polarimeter, the solenoid for producing the magnetic field, and the spectrograph.

The light source was a 15-kV a.c. spark operating between tungsten-steel electrodes. This source was found satisfactory in respect of several requirements, *e.g.* the continuity of spectrum, its high intrinsic brightness, freedom from wandering, and its uniform intensity over the spark gap. The power was supplied

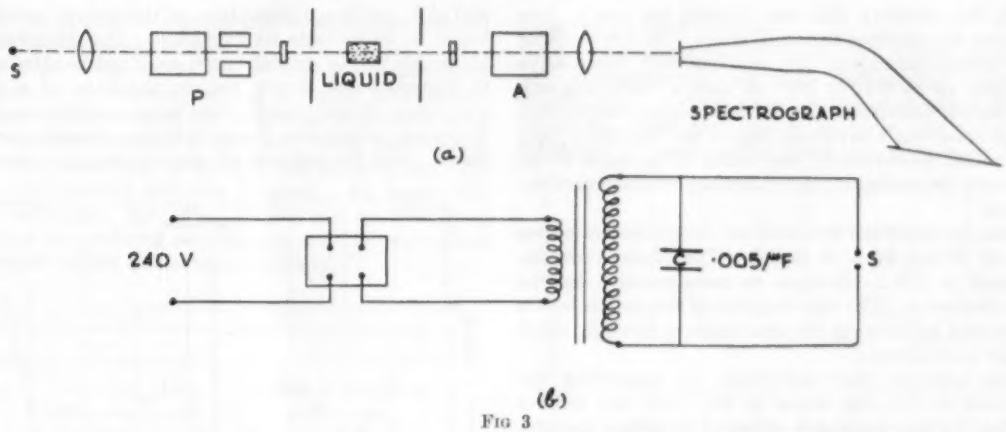


FIG 3

EXPERIMENTAL ARRANGEMENT: (*a*) OPTICAL LAY-OUT; (*b*) SPARK SOURCE ELECTRICAL CIRCUIT

from 230-volt a.c. mains through a step-up transformer, with a 0·005-μF condenser in parallel with the source (Fig 3 (*b*)). The positioning of the light source to produce uniform intensity of light in the fields of the polarizer was originally carried out photographically, but later the use of an eyepiece in front of the analyser disk was found to be equally satisfactory.

The polarizer was a Lippich quartz three-field instrument with a Foucault prism and a variable half-shadow angle of 15° max. The analyser was graduated to 0·2° and, by means of a vernier, rotations could be measured to 0·01° and estimated to 0·005°.

The magnetic field was produced by a solenoid originally designed [9] to give a field strength of 4000 Gauss at 16 amp. The current was supplied by 440-volt d.c. mains, and regulated by a variable resistance in parallel with the solenoid, using a precision meter with an accuracy of $\pm$0·02 amp. The solenoid was cooled by a stream of air from a blower situated outside the laboratory. The temperature of the polarimeter tube was adjusted to 20° C $\pm$ 0·1° by circulating thermostated water through the jacket, housing the tube inside the solenoid. Since short polarimeter tubes were employed, the field strength was substantially increased by packing the solenoid cores with mild steel plugs. Two sets of two concentric plugs were used. The outer ones were so drilled as to accommodate the inner two, which themselves had a longitudinal $\frac{1}{2}$-inch hole to allow the passage of light.

Preliminary measurements with a 2-cm polarimeter cell, whilst giving some evidence of anomalous magnetic rotation, indicated the need for a much shorter cell. More concentrated solutions could then be used to enhance the solute contribution to the total rotation. The cell finally developed (Fig 4) was made of stainless steel, and had an annular spacing which could hold a few drops of solution to give a layer 1·143 mm in thickness. The solution could be trapped between two quartz windows which were held in position by two threaded caps. Rubber spacers were used to avoid any strain on the quartz disks.

The spectrograph was a standard Hilger "medium quartz" instrument with a spectral range 2000–10,000 Å.

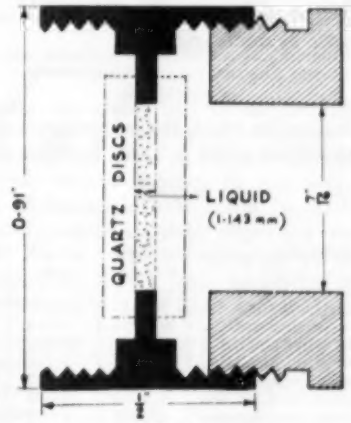


FIG 4

LONGITUDINAL SECTION OF MICRO-POLARIMETER TUBE

EXPERIMENTAL

The technique for measuring the magneto-optical rotation dispersion photographically was based on reading the wavelength or wavelengths of the match points, *i.e.* the points where the three fields of the polarizer were of equal intensity, for a particular setting of the analyser disk.

A parallel beam of light was polarized, and then passed through the sample along the magnetic field (Fig 3 (*a*)). The emergent radiation, after having passed through the analyser, was focused on the slit of the spectrograph. Ample time was given for the sample to reach the temperature of 20° C. The analyser was then so set that the rotation corresponded to a wavelength of about 5000 Å. Then visual setting could be carried out by examining the image of the three fields of the polarizer on the slit of the spectrograph. The exposures were then started, and after

each, the analyser disk was rotated by one or two degrees and another exposure made. In approaching the absorption region, the analyser disk was always stepped up by 0·1° or 0·2°, so that if there was any anomalous behaviour it could not escape observation. In or near the absorption region the exposure time was raised considerably, very often of the order 30–45 minutes, depending on the extinction coefficient of the solute.

The spectra were recorded on Ilford–Zenith plates (Hand D700), 10 × 4 inches. The plates were developed in I.D.2 developer as recommended by the manufacturer. The wavelengths of the match points were read by viewing the spectrogram through a low power microscope.

The solenoid was calibrated by measuring the rotation of CO_2-free water at 20° C for the sodium D-line (for this purpose a constant deviation spectrometer was employed). The value of 0·013086 for the Verdet constant given by Rodgers and Watson [10] was used in the calculations. With a current of 15 amp through the solenoid, the rotation of a 2-cm layer of water was 3·0550, indicating a field strength of 7004 Gauss. All subsequent measurements were made with this magnetic field strength.

RESULTS

The solutions for which the magnetic rotation have been measured are given in Table I, which also shows

TABLE I

Solutions	Conc. g/litre solution	Length of cell, mm	Reference
Benzene in *cyclo*hexane .	0·3017	20·000	Fig 7
Benzene in *cyclo*hexane .	21·4824	1·143	Fig 8
Camphor in ethyl alcohol .	3·8944	20·000	Fig 6
Camphor in ethyl alcohol .	60·4046	1·143	Fig 9
Anthracene in benzene .	1·4022	1·143	Fig 10
*cyclo*Hexanone in *n*-hexane	4·1840	20·000	Fig 5 (*a*)
*cyclo*Hexanone in *n*-hexane	8·2960	6·402	Fig 5 (*b*)
*cyclo*Hexanone in *n*-hexane	20·3192	1·143	Fig 11 (*a*)
1,2,4-Trichlorobenzene in *cyclo*hexane . . .	8·2488	1·143	Fig 11 (*b*)

the concentration of the solutions and the cell length employed in the observations. The figures where the corresponding dispersion curves appear are given in Column 4. In all cases, the absorption curves are drawn by broken lines on the same diagram.

Measurements with the 2-cm cells failed to show definitely the existence of any anomalous behaviour in the absorption region. Thus, for example, the distribution of points on the rotation dispersion curve of benzene in *cyclo*hexane (Fig 7) is of little evidence to prove the existence of an anomalous Faraday effect. Fig 7 also gives the rotation dispersion of benzene (B.D.H. extra pure) in the range 4470–2842 Å. Previous measurements by Preiswerk [11] are down to 2894 Å. Although there is little evidence of the presence of any anomalous effect in the rotation dispersion curve of *cyclo*hexanone in benzene (Fig 5 (*a*) and (*b*)), yet the distribution of the points could be taken as to indicate its existence. The deviation of the points from a smooth curve could not be attributed to experimental errors, for, in the case of a non-absorbing liquid under the same conditions, the dispersion points were found to lie on a smooth normal curve. For the solution of camphor in ethyl alcohol,

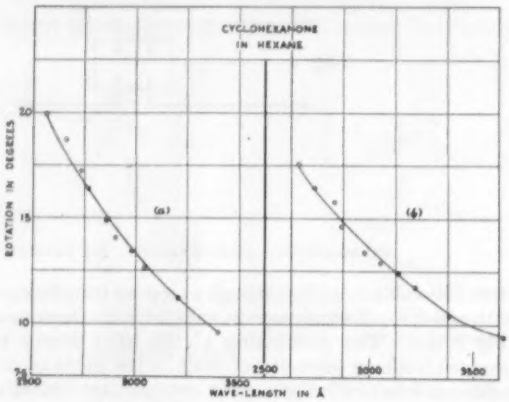


FIG 5

ULTRA-VIOLET ROTATION DISPERSION CURVES FOR *CYCLO*-HEXANONE IN HEXANE (LONG CELLS)

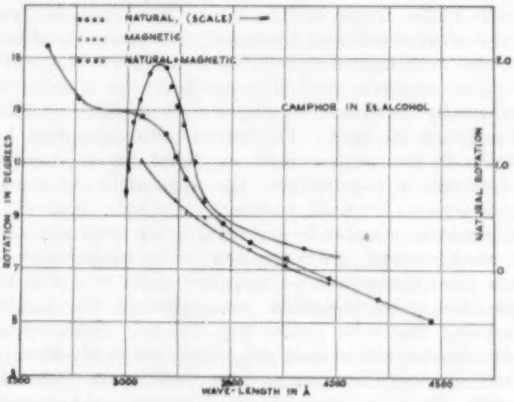


FIG 6

ULTRA-VIOLET ROTATION DISPERSION CURVE FOR CAMPHOR IN ETHYL ALCOHOL (LONG CELLS)

the magnetic rotation as well as the natural was measured. The magnetic contribution to the total effect was arrived at in the following manner: if

α = Magnetic rotation of the sample,
μ = Magnetic rotation of the cell,
β = Natural rotation of substance + cell.
γ = Natural rotation of the cell, and
A = Total magnetic and natural rotation.

then $\alpha = A - \mu - (\beta - \gamma)$

In Fig 6 it is interesting to note how the dispersion curve of the combined effect (natural + magnetic)

tends to acquire a normal course after the natural effect has been subtracted.

In none of the above cases could the existence of an anomalous Faraday effect be really established. Further elaboration of the technique of measurement was therefore needed before any such justification could be made, and it was for this purpose that the micro-polarimeter cell was designed. By employing this technique, the effect of solvent on the total rotation was reduced considerably and the anomalous behaviour of the solute thus enhanced.

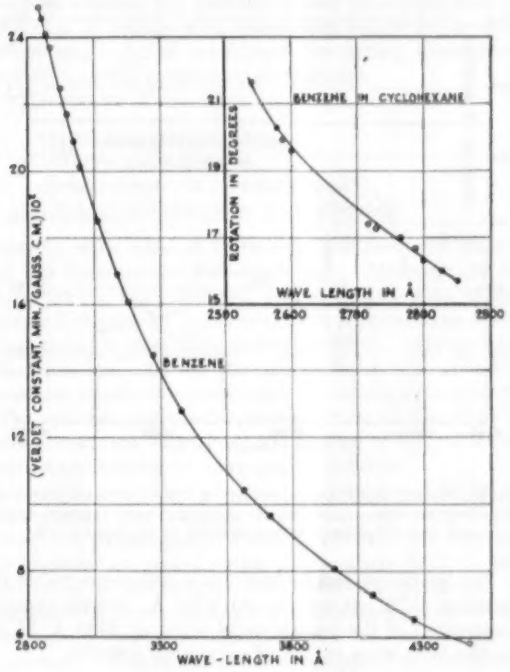


FIG 7

ULTRA-VIOLET ROTATION DISPERSION CURVES FOR BENZENE IN *cyclo*HEXANE AND FOR PURE BENZENE (LONG CELLS)

Benzene in cyclo*Hexane*

For benzene in *cyclo*hexane the first absorption band covers approximately the region 2630–2605 Å, and the second the region 2585–2537 Å. The short-wave transmission cut-off was at about 2520 Å. By proper adjustment of the analyser disk it was possible to measure the rotation close to both sides of the absorption bands and also in the range 2605–2585 Å. In practice, limitations were introduced by the fact that at the match point the intensity of radiation was at its minimum. This difficulty was overcome, as far as possible, by increasing the exposure time.

The rotation dispersion curve is presented in Fig 8. The absorption curve of benzene reproduced on the same graph is the result of measurements by N.B.S. (API Research Project 44, No. 1, 1945). The maximum value of rotation occurs at 2645 Å, about 100 Å on the long wavelength region of maximum absorption.

Camphor in Ethyl Alcohol

The concentration of about 60 g/litre used in the measurements, afforded reasonable spectral transmission on both sides of the absorption band. Inside the absorption region, however, the radiation reaching the photographic plate was very weak, and

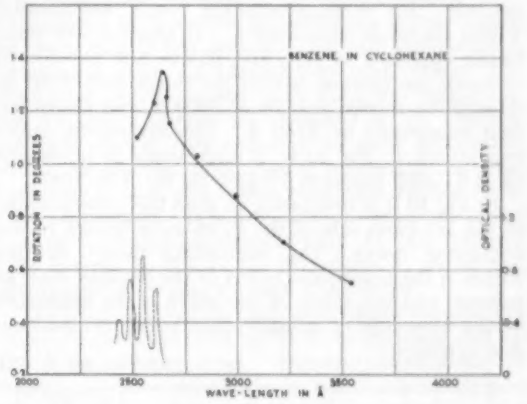


FIG 8

ULTRA-VIOLET ROTATION DISPERSION AND OPTICAL DENSITY CURVES FOR BENZENE IN *cyclo*HEXANE (SHORT CELL)

consequently the plates had to be somewhat over-developed. The process of development was not allowed to continue so far as to cause diffusion of the image at the match points. In this way, a faint recording of the triple field could be made. Both natural and magneto-optical dispersion curves are shown in Fig 9. The wavelengths of maximum natural rotation (1·36°) and maximum magneto-optical rotation (0·4°) are 3145 and 3090 Å respec-

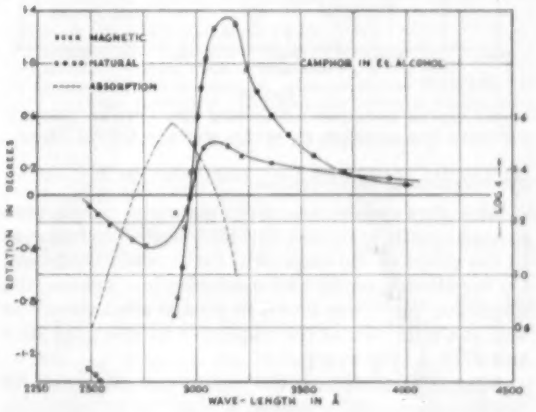


FIG 9

ULTRA-VIOLET ROTATION DISPERSION AND OPTICAL DENSITY CURVES FOR CAMPHOR IN ETHYL ALCOHOL (SHORT CELL)

tively, the difference being 55 Å. The magneto-optical dispersion curve changes sign at 2977 Å and the natural dispersion at 2967 Å. The absorption of camphor in ethyl alcohol (M/100) has been measured by Lowry and French.[12] It is from their data that the

absorption curve is reproduced here. The wavelength of maximum absorption is 2880 Å, about 175 Å less than the wavelength of maximum magneto-optical rotation.

Anthracene in Benzene

Anthracene has a relatively high extinction coefficient. Its three absorption bands are located within the range 3800–3300 Å. In practice, the three bands appeared as one, and it was not possible to measure the rotation within the range 3875–3130 Å. Absorption started sharply at 3800 Å, and the radiation reappeared at 3140 Å. The absorption curve reproduced in Fig 10 is of anthracene in *iso*-octane (N.B.S., API Research Project 44, No. 170, 1947).

In Fig 10 it is interesting to note the convex shape of the left-hand side of the short-wave branch of the dispersion curve. The controlling factor in this region is the absorption bands of the benzene used as solvent, and the shape of the curve is the indication of the approach of another anomalous phenomenon due to this.

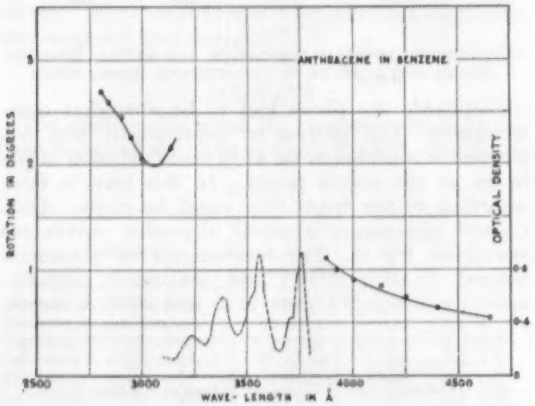


FIG 10

ULTRA-VIOLET ROTATION DISPERSION AND OPTICAL DENSITY CURVES FOR CAMPHOR IN ETHYL ALCOHOL (SHORT CELL)

cyclo*Hexanone in* n-*Hexane*

With pure *cyclo*hexanone the measured points were so haphazardly scattered that no definite conclusion as to the shape of the dispersion curve could be drawn. On the other hand, as with a solution in *n*-hexane, the dispersion curve was found to possess a maximum as well as a minimum at the respective wavelengths 3015 and 2775 Å (Fig 11 (*a*)).

Allsopp [13] measured the refraction dispersion of *cyclo*hexanone, and observed a ripple in its refraction curve. The absorption curve of *cyclo*hexanone reproduced is from Herold's [14] data. The maximum absorption occurs at 2896 Å, while the maximum rotation is at about 3020 Å.

1,2,4-*Trichlorobenzene in* cyclo*Hexane*

The position of the absorption band and the extent of absorption of this substance afforded reasonable possibility of measuring its magnetic rotation through its absorption region. The absorption curve presented in Fig 11 (*b*) is the work of Wolf and Strasse.[15]

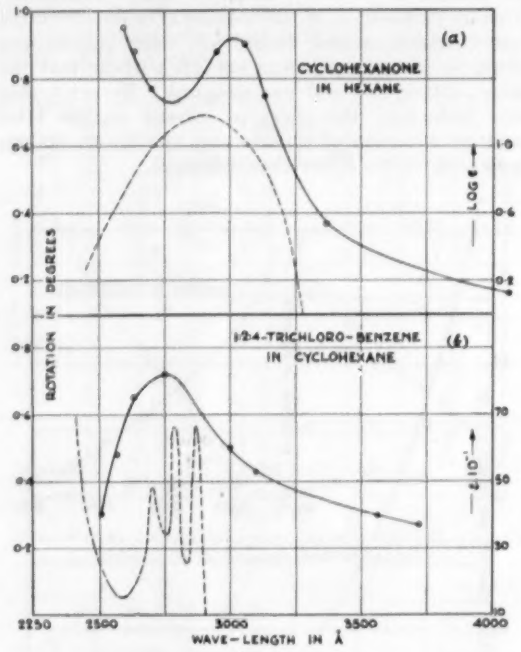


FIG 11

ULTRA-VIOLET ROTATION DISPERSION AND OPTICAL DENSITY CURVES FOR *cyclo*HEXANONE IN HEXANE (SHORT CELL) AND FOR 1,2,4-TRICHLOROBENZENE IN CYCLOHEXANE

The graphical results indicate a maximum value of rotation (0·72°) at wavelength 2750 Å; the maximum absorption of the central band being at 2785 Å, 35 Å on the long-wave region of maximum rotation.

DISCUSSION

The measurements of magneto-optical dispersion in the absorption regions, that have been recorded, have been made in order to illustrate the existence of anomalous behaviour and also to provide a guide for future studies regarding this phenomenon. The discussion that follows is an attempt to correlate the results qualitatively and treat them in the light of the theories underlying the Faraday effect.

Magneto-optical rotation has been used widely in mixture analysis. No attempt is made here to discuss the deviations from the mixture rules as the wavelengths of absorption are approached. For ideal mixtures, the rules have usually been found to be valid in the transparent region.

From the theoretical outline that has already been considered, it is seen that the controlling factor in the dispersion of magnetic rotation, more especially as the absorption region is reached, is the frequency or frequencies of the oscillator. The quadratic equation,

$\alpha d^2 = \text{const.}$, originally due to Hallo,[16] has been confirmed not only for the D-line of sodium vapour but also for other absorption lines. In this equation α is proportional to the angle of rotation and d proportional to the difference between the measuring frequency and the frequency of absorption.

However, Zeeman's description of magneto-optical rotation applies only to individual spectral lines, and a rigorous analysis of the experimental data will have to take into account the contributions made to the observed rotation by each absorption line. For substances which possess selective absorption lines, *e.g.* sodium vapour, the problem would be simple, but in the case of liquids with absorption bands the overall effect can only be considered by taking absorption maxima as the controlling frequencies.

The results of measurements on :

benzene in *cyclo*hexane,
anthracene in benzene,
*cyclo*hexanone in *n*-hexane, and
1,2,4-trichlorobenzene in *cyclo*hexane

comply with what is to be expected from the theory of the diamagnetic Faraday effect. Although, to be more exact, the effect due to the contribution of the solvent should be considered, yet if such were done, it is unlikely that the conclusions would undergo any modification. In all the above cases, the rotation remains positive on both sides of the absorption band. The symmetry of the dispersion curves on the edges of the absorption bands and the change of sign of $d\alpha/d\lambda$ are characteristic of diamagnetic rotation.

Camphor in ethyl alcohol has been found to be an exception. Its rotation dispersion curve represents that of a paramagnetic Faraday effect. The rotation is positive at wavelengths longer than 2977 Å and negative on the shorter side. The change of sign of rotation in going through the inflexion point of the dispersion curve is characteristic of paramagnetic rotation. This does not always happen, as sometimes a high value of the A-term may shift the whole curve to the positive side of the co-ordinates. Mischer [17] has concluded that the existence of an anomalous natural rotation does not necessarily imply an abnormal magneto-optical dispersion for naturally rotating substances. His observations are based on measurements on solutions of camphor–quinone, dithiourethan of *l*-borneol, and benzalcamphoryledon-3-acetone, and refer to absorption bands in the visible region. Pfleiderer,[18] on the other hand, working on solutions of camphorquinone and diphenylmethylene camphor had earlier come to the opposite conclusions.

For benzene and anthracene a rigorous analysis would need a study of rotation dispersion adjacent to individual absorption maxima. Theoretically, to each maximum absorption, these should correspond with a maximum rotation. If such be the case in practice, then the dispersion curve of anthracene (Fig 10) should include maximal rotations corresponding to each absorption maximum in the region 3875–3175 Å. The same argument can also be regarded to apply to benzene and 1,2,4-trichlorobenzene. For camphor (Fig 9) and *cyclo*hexanone (Fig 11 (*a*)) the dispersion curves, after having reached a maximum value, descend and go through a minimum value as absorption begins to decrease. The absorption of these substances possesses only one maximum. When compared to this, the above may be taken to indicate that each absorption maximum, *i.e.* each oscillator or a harmonious combination of oscillators, is responsible for each peak in the dispersion curve. For benzene, anthracene, and 1,2,4-trichlorobenzene, where the absorption curves possess more than one maximum, the dispersion curves are expected to go through maximal values corresponding to each absorption peak. In practice, difficulties in measuring the rotation close to each absorption maximum did not allow such verification. It is interesting to note how in the case of 1,2,4-trichlorobenzene (Fig 11 (*b*)) rotation falls sharply in the range 2675–2480 Å, where the absorption curve goes through a minimum.

The position of maximum rotation leads the position of maximum absorption by 55 Å for camphor and by 125 Å for *cyclo*hexanone. Benzene shows a similar lead in dispersion relative to its maximum absorption (97 Å). For other substances investigated, the graphical data are not sufficient to assess this lead. This difference in wavelengths may probably be attributed to a difference in nature or state of the active electrons responsible for the two phenomena, or it may correspond to a lag in oscillations. However, until further data are obtained, preferably on one-component systems, no conclusive assertions can be made regarding the significance of this lead or even its universality.

References

[1] Faraday, M. *Phil. Trans.*, 1846, **3**, 1; *Phil. Mag.*, 1846, **28** (3), 294.
[2] Drude, P. "Lehrbuch der Optik."
[3] Dorfman, J. *Z. Phys.*, 1923, **17**, 98.
[4] Cotton, A. *Ann. Chim. (Phys.)*, 1896, **8** (7), 347.
[5] Cotton, A., and Scherer, M. *Compte Rendu*, 1932, **195**, 915 and 950; Scherer, M., and Cordinier. *Compte Rendu*, 1932, **196**, 1724.
[6] Cotton, A., and Scherer, M. *Compte Rendu*, 1932, **195**, 1342.
[7] Wood, R. W. *Phil. Mag.*, 1905, **10** (6), 408; 1907, **14**, 145.
[8] Wood, R. W. *Phil. Mag.*, 1905, **9** (6), 725.
[9] Tadayon, J., Nissan, A. H., and Garner, F. H. *Analyt. Chem.*, 1949, **21**, 1532.
[10] Rodgers, J. W., and Watson, W. *Z. phys. Chem.*, 1896, **19**, 323.
[11] Preiswerk, P. *Helv. phys. acta.*, 1934, **7**, 203.
[12] Lowry, T. M., and French, H. S. *J. chem. Soc.*, 1924, **125**, 1921; Lowry and Southgate. *J. chem. Soc.*, 1910, **97**, 907.
[13] Allsopp. *Proc. roy. Soc.*, 1934, **A146**, 307.
[14] Herold, W. H. *Z. phys. Chem.*, 1932, B**18**, 265.
[15] Wolf, K. L., and Strasse, O. *Z. phys. Chem.*, 1933, **B21**, 389.
[16] Hallo, J. *Z. Phys.* 1903, **4**, 545.
[17] Mischer, E. *Helv. phys. acta.*, 1930, **3**, 93.
[18] Pfleiderer, W. *Z. Phys.*, 1926, **39**, 663; Hagenbach, A., and Pfleiderer, W. *Arch. Sci. Phys. nat.*, 1926, **8** (5), 262.
[19] Ladenburg, R. *Z. Phys.*, 1925, **34**, 898; *Z. Phys.*, 1927, **46**, 168.
[20] Wood, R. W. "Physical Optics," 3rd Ed., New York: Macmillan and Co. Ltd., 1934.

PART II. MAGNETO-OPTICAL ANALYSIS OF HYDROCARBON MIXTURES*

By A. LABBAUF, C. W. NUTT, and F. H. GARNER, O.B.E.

SUMMARY

The magneto-optical rotation dispersion of twelve naphthenes have been measured in the spectral range 4600–2550 Å and the results given in graphical form. The magneto-optical dispersion of water has also been given in the range 6000–2500 Å.

Magneto-optical aids to mixture analysis have been briefly reviewed. In the ultra-violet region divergence takes place in the dispersion of hydrocarbons, which may be used for the analysis of hydrocarbon mixtures not susceptible of analysis in the visible region. A method for structural analysis of mixtures of low molecular weight alkanes and their methyl isomers has been proposed and, in particular, the use of the magneto-optical constant, D, is suggested for control in fractionating a mixture of these hydrocarbons to constant molecular weight fractions. An empirical formula connecting D and the ratio of side-chain carbon atoms to total carbon content of naphthenes has been set up.

INTRODUCTION

THE magneto-optical rotation has been widely applied to the analysis of hydrocarbon mixtures, and in parallel with refractometric methods it has gained considerable importance in the evaluation of hydrocarbon blends.[1,2,3] The aim of this work has been to study the dispersion behaviour of hydrocarbons in the ultra-violet region, with special reference to magneto-optical methods of analysis of hydrocarbon mixtures involving components which have five- and six-membered saturated rings.

The experimental results reported for twelve hydrocarbons, six of which are *cis-* and *trans*-isomers of dimethyl*cyclo*hexane, were insufficient in themselves, and therefore in the discussions that follow, recourse has been made to data obtained by Foehr and Fenske,[4] Waterman,[5] and Tadayon and Garner.[3]

TABLE I

Density and Refractive Indices

Substances	Density, d_4^{20}	Refractive index		
		4359 Å	5461 Å	5893 Å
trans-1,2-Dimethylcyclohexane	0·7766	1·43680	1·42887	1·42705
cis-1,2-Dimethylcyclohexane	0·7983	—	—	1·43630
trans-1,3-Dimethylcyclohexane	0·7682	1·43283	1·42517	1·42343
cis-1,3-Dimethylcyclohexane	0·7919	1·44165	1·43396	1·43197
trans-1,4-Dimethylcyclohexane	0·7623	1·43048	1·42278	1·42135
cis-1,4-Dimethylcyclohexane	0·7843	1·43949	1·43168	1·42996
*cyclo*Hexane	0·7740	1·42575	1·42807	1·42645
n-Propylcyclohexane	0·7934	1·44677	1·43879	1·43710
Methylcyclopentane	0·7508	1·41939	1·41146	1·41015
Ethylcyclopentane	0·7681	—	—	1·43042
n-Propylcyclopentane	0·7731	—	—	1·42695
iso-Propylcyclopentane	0·7781	1·43529	1·42887	1·42655

The present measurements have been made in wavelength regions for which no report is so far available in the literature. Measurements were made at 20° C with a standard Hilger polarimeter tube 2 cm long, and with a magnetic field strength of 7000 Gauss. The apparatus and the technique of measurement have been discussed in a previous paper.[6] The refractive indices of the hydrocarbons were measured by a Pulfrich refractometer and the densities by the pyknometer method. The results are shown in Table I.

RESULTS

The magneto-optical rotation dispersion of twelve hydrocarbons has been measured in the wavelength region 4600–2550 Å, and the results have been recorded graphically in Figs 2 to 7. The results of measure-

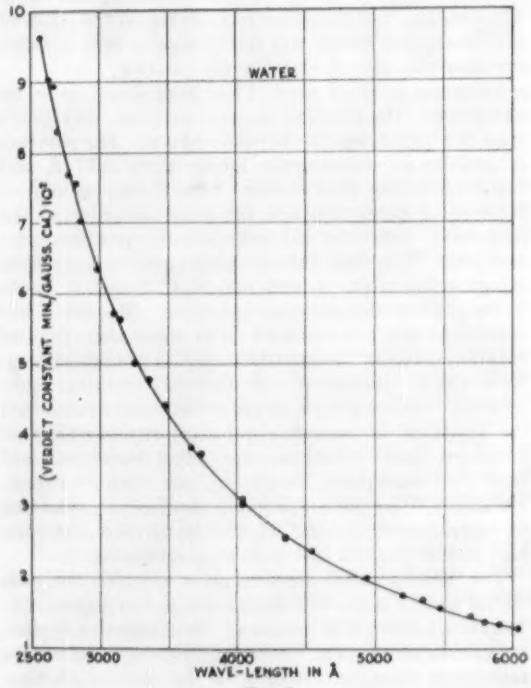


FIG 1

ULTRA-VIOLET VERDET CONSTANT FOR WATER: ○ THIS WORK, AND ● ROBERTS'[7] WORK

* MS received 22 March 1955.

ments on CO_2–free water at various wavelengths are shown in Fig 1, which also shows, for comparison, the results obtained by Roberts.[7]

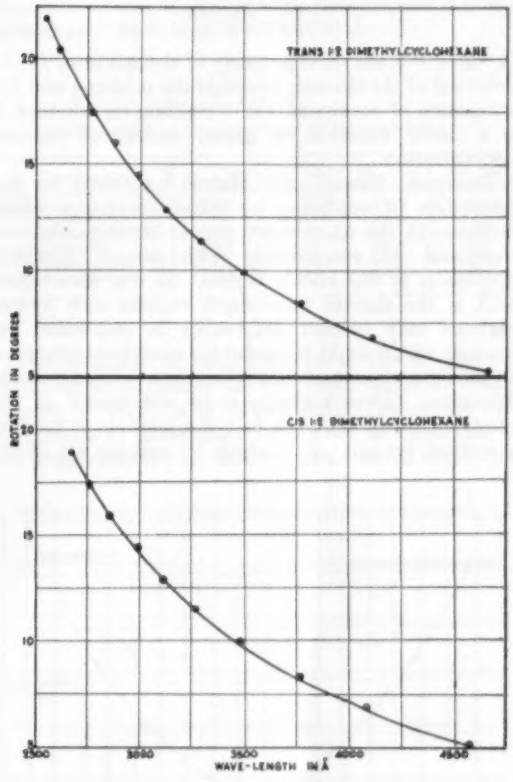


FIG 2

ULTRA-VIOLET ROTATION DISPERSION FOR *CIS-* AND *TRANS-*1,2-METHYL*CYCLO*HEXANE

Numerical values for the Verdet constant, V, of the hydrocarbons for the mercury line 4359 Å were estimated directly from the dispersion curves. Table II contains values for the dispersion, V_{4359}/V_{5461}, and the Verdet constants for three wavelengths. Verdet constants at the longer wavelengths were estimated as follows: Several plots of V and $1/V$ *v.*

TABLE II

Dispersion and Verdet Constants

Substances	V_{4359}/V_{5461}	Verdet const. 10^5 min/Gauss cm		
		4359 Å	5461 Å	5893 Å
trans-1,2-Dimethyl*cyclo*hexane .	1·586	2·528	1·594	1·234
cis-1,2-Dimethyl*cyclo*hexane . .	1·636	2·447	1·495	1·291
trans-1,3-Dimethyl*cyclo*hexane .	1·647	2·571	1·561	1·356
cis-1,3-Dimethyl*cyclo*hexane . .	1·561	2·524	1·617	1·332
trans-1,4-Dimethyl*cyclo*hexane .	1·603	2·601	1·623	1·372
cis-1,4-Dimethyl*cyclo*hexane . .	1·563	2·412	1·534	1·273
*cyclo*Hexane	1·643	2·357	1·434	1·243
n-Propyl*cyclo*hexane . . .	1·627	2·526	1·552	1·333
Methyl*cyclo*pentane . . .	1·636	2·421	1·489	1·277
Ethyl*cyclo*pentane . . .	1·706	2·443	1·432	1·289
n-Propyl*cyclo*pentane . . .	1·642	2·498	1·521	1·318
iso-Propyl*cyclo*pentane . .	1·644	2·516	1·530	1·370

TABLE III

Comparison of Results

(V_{4359}/V_{5893}) average = 1·895

Substances	$V_{4359} \cdot 10^2$ measured	$V_{4359} \cdot 10^2$ calculated
Methyl*cyclo*pentane . .	2·421	2·405
Ethyl*cyclo*pentane . .	2·443	2·456
n-Propyl*cyclo*pentane . .	2·498	2·488
iso-Propyl*cyclo*pentane . .	2·516	2·515
*cyclo*Hexane	2·357	2·361 *
Benzene	6·160	6·201 *

* Measured by Foehr.[4]

various functions of λ were made for each hydrocarbon, and it was found that the plots of $1/V$ against λ^2 gave the best fit. This indicated that the dispersion is governed by an equation containing more than one term. The values of V_{4359}/V_{5461}, and V_{5641} given in Table II were found by extrapolation of the lines

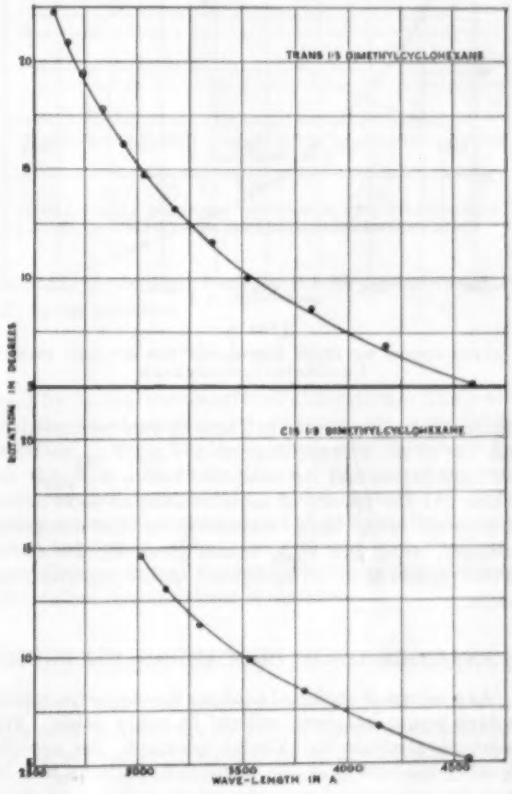


FIG 3

ULTRA-VIOLET ROTATION DISPERSION FOR *CIS-* AND *TRANS-*1,3-DIMETHYL*CYCLO*HEXANE

representing $1/V$ *v.* λ^2. Foehr, Fenske, *et al* have measured the magnetic rotation of a large number of hydrocarbons, and have given individual values as well as average figures of V_{4358}/V_{5461}, V_{4359}, V_{5893}, and V_{5461}/V_{5893} for alkanes, alkenes, and naphthenes. The

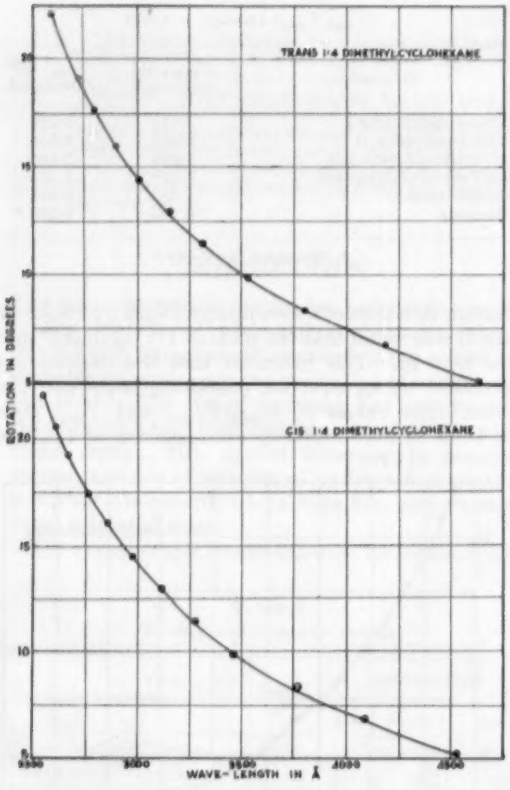


FIG 4

ULTRA-VIOLET ROTATION DISPERSION FOR *CIS-* AND *TRANS-*1,4-DIMETHYL*CYCLO*HEXANE

figures of V_{5893} recorded in Table II were estimated by the use of the average dispersion $V_{4359}/V_{5893} = 1{\cdot}895$ for naphthenes and the measured values of V_{4359}. In Table III the results of measurement at 4359 Å are compared with those estimated in the foregoing manner, using the V_{5893} values given by the above workers, and show an agreement within experimental error.

ANALYSIS OF HYDROCARBON MIXTURES

As a means of chemical analysis the magneto-optical rotary power has been utilized in many fields. For mixture analysis the Verdet constant, the specific Verdet constant, V/d, the molecular rotation, $M.V/d$, and the constant of magneto-optical rotation as given by

$$D = 9n/(n^2 + 2)^2.M/d.V$$

have been employed by several workers,[2,3,5] each on the basis of its additive character under certain conditions. In general, the equations employed in these analyses are all of the same form, *i.e.*

$$P = \sum_i P_i.f(c),$$

in which P is the total property of the mixture, P_i the property of the ith component of the mixture, and $f(c)$ a function of concentration depending on whether P is a linear function of gram, molar, or volume concentration.

Tadayon, Nissan, and Garner[3] referred to the possibility of analysing by purely magneto-optical methods in the ultra-violet region, ternary mixtures composed of components with almost identical dispersion in the visible region. It was maintained that in the shorter wavelength regions such hydrocarbons may exhibit differences in dispersion behaviour which could be useful for analytical purposes. In the light of present data it has been noticed that the dispersion curves undergo some divergence in the ultra-violet region and, in fact, it is possible to develop a method for mixture analysis by making use of the

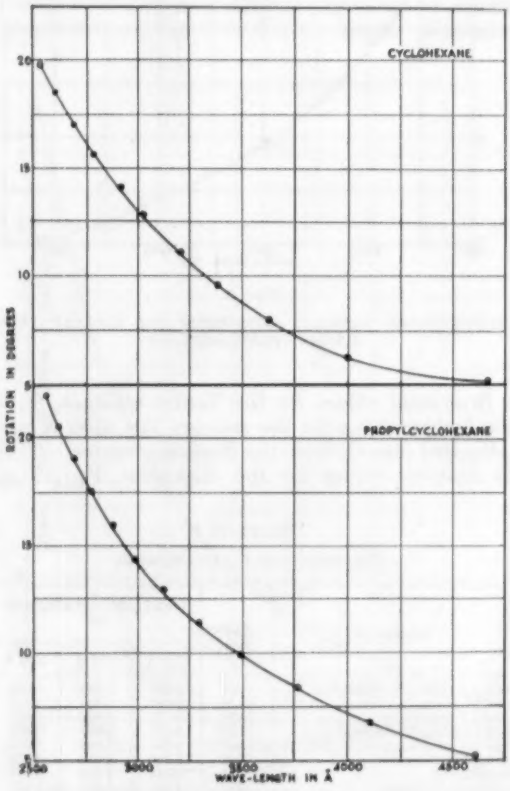


FIG 5

ULTRA-VIOLET ROTATION DISPERSION FOR *CYCLO*HEXANE AND PROPYL*CYCLO*HEXANE

wider differences that exist among the Verdet constants of its components. The data representing some of the hydrocarbons investigated are recorded in Table IV. It is noted that ΔV, the difference in Verdet constants of each pair of hydrocarbons, is much greater at 2750 Å than it is at 4250 Å.

TABLE IV

Divergence in the Dispersion of Hydrocarbons

Substance	$V_{2750} \cdot 10^3$	$\Delta V \cdot 10^3$	$V_{4250} \cdot 10^3$	$\Delta V \cdot 10^3$
*cyclo*Hexane . . .	6·912	—	2·442	—
n-Propylcyclohexane .	7·769	−0·857	2·678	−0·236
Methylcyclopentane. .	7·242	0·527	2·571	0·107
Ethylcyclopentane . .	8·463	−1·221	2·614	−0·043
n-Propylcyclopentane .	8·141	0·322	2·742	−0·128
iso-Propylcyclopentane .	7·713	0·428	2·721	0·021

The accuracy of such analysis in the short-wave region depends mainly on the proper choice of wavelengths at which it is carried out. The extent and magnitude of the relative divergence in dispersion in the ultra-violet region of components which make up a

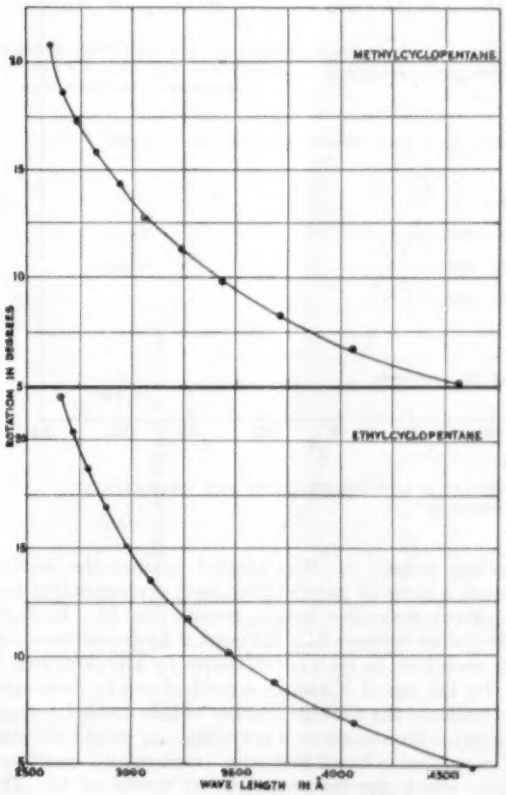


FIG 6

ULTRA-VIOLET ROTATION DISPERSION FOR METHYLCYCLOPENTANE AND ETHYLCYCLOPENTANE

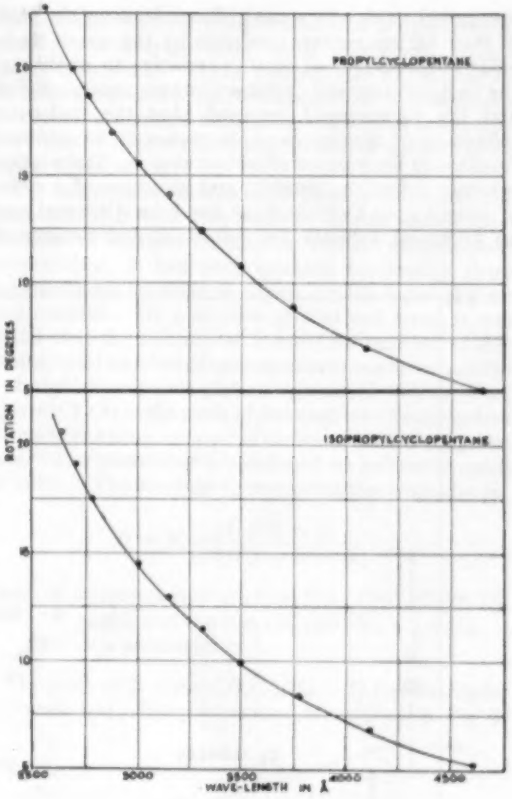


FIG 7

ULTRA-VIOLET ROTATION DISPERSION FOR PROPYLCYCLOPENTANE AND *ISO*PROPYLCYCLOPENTANE

mixture is governed both by the dispersion constant, K, in the equation

$$\alpha = \sum_k \frac{K}{\lambda^2 - \lambda_k^2}$$

and by λ_k, the wavelength of absorption. The wavelengths most suitable for carrying out a particular mixture analysis are those which offer maximum use of the ΔVs. In particular, if the mixture contains unsaturated components, which absorb at lower frequencies, the correct choice of wavelengths becomes very important. Thus, prior to any such analyses a complete survey of the magneto-optical dispersion of individual hydrocarbons is essential.

STRUCTURAL GROUP OR TYPE ANALYSIS

In the study of hydrocarbon mixtures, it is often desirable to know the average number of characteristic or structural groups/molecule of the mixture. The use of magneto-optical rotation, together with refractometric methods of analysis, is gaining considerable importance for this purpose, but as yet the latter has enjoyed more practical application. Foehr [4] has

attempted to classify some hydrocarbons on the basis of their carbon content/molecule by the use of molecular magneto-optical rotation relative to water and the magneto-optical rotatory water ratio. Egloff and his co-workers [8] reported that the molecular refraction of mononuclear aromatics is an additive function of the number of carbon atoms. The relation between refraction, density, and structure of a series of homologous hydrocarbons has been discussed and an empirical formula for refraction and density of

have shown that the increase in Verdet constant/(*iso*-methyl group/total number of carbon atoms) of low molecular weight alkanes and their methyl isomers remains constant for isomeric hydrocarbon alkanes and does not change with changes of structure.

For *n*-alkanes and their methyl isomers, the magneto-optical rotation constant D also shows a regular variation with structure. Its value increases gradually with the number and position of the side methyl groups, and it shows a linear relationship with

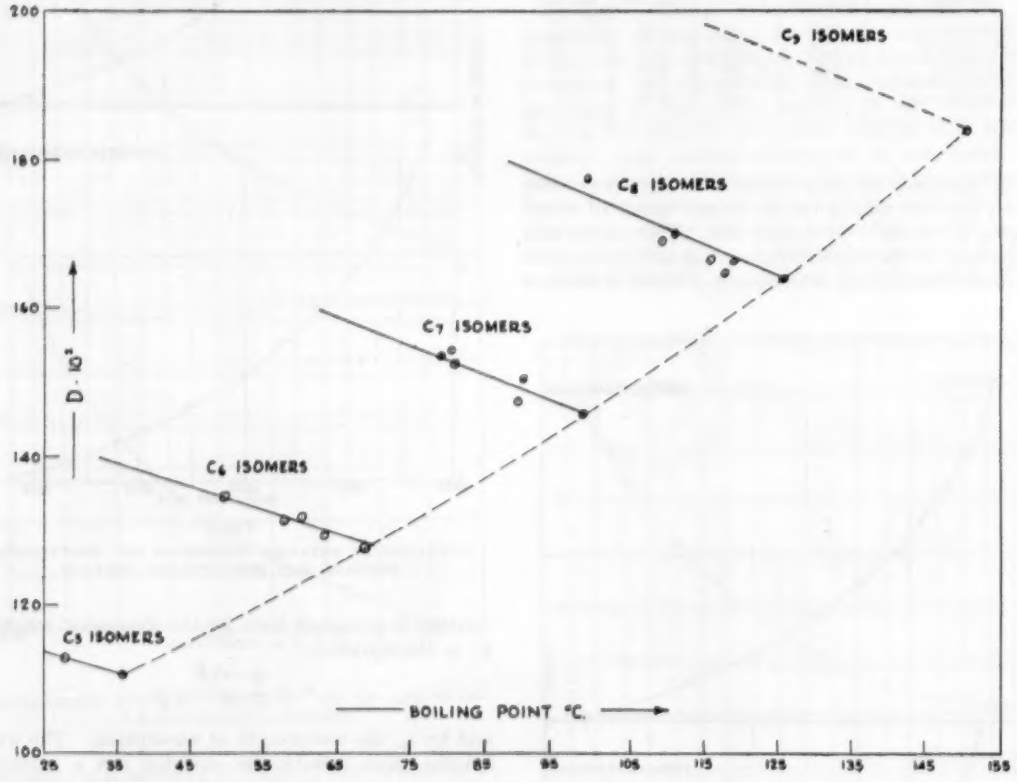


FIG 8

RELATION BETWEEN THE MAGNETO-OPTICAL ROTATION CONSTANT D AND BOILING POINT FOR *N*-ALKANES AND THEIR METHYL ISOMERS

n-alkanes and α-alkenes been given by Smittenberg and Mulder.[9] The same authors have also reported the refraction and density of alkyl*cyclo*pentanes and alkl*cyclo*hexanes.[10] In all such studies attempts are always made to attribute unvarying properties to the functional groups by means of which differentiation could be made when the groups occur under various structural conditions.

The Verdet constant, in certain circumstances, shows additive properties which can be used for analytical purposes. In certain other circumstances the constant of magneto-optical rotation, D, acquires additive properties. Westerdijk and Waterman [5] boiling point. If D is plotted against the boiling point, a series of parallel lines, each corresponding to a constant molecular weight, results (Fig 8). In Fig 8 the points representing the normal hydrocarbons, one on each line, lie on a curve shown by a broken line.

By the use of V and D, a method can be developed to estimate the average number of side methyl groups/molecule for a mixture of low molecular weight alkanes. The method is based first on a " molecular " fractionation, which can be controlled by means of D. The mixture to be analysed is first fractionated to constant molecular weight portions and the Verdet constant of each fraction measured. The value of V of each

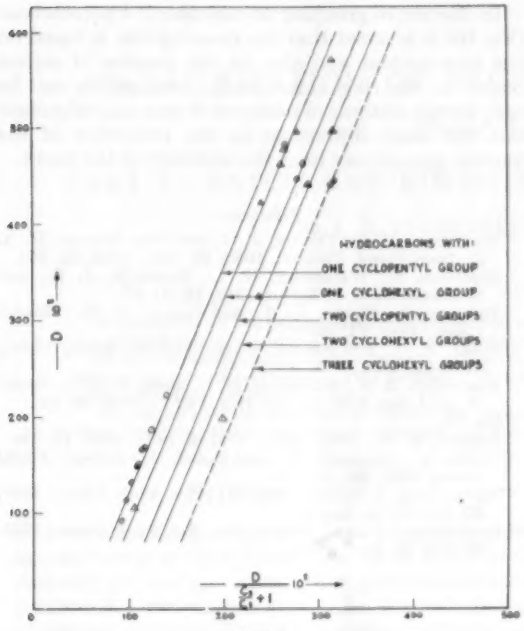


FIG 9

RELATION BETWEEN THE MAGNETO-OPTICAL ROTATION CONSTANT D AND THE STRUCTURE OF ALKYL*CYCLO*PENTANES AND ALKYL*CYCLO*HEXANES

fraction can then be transformed into a figure representing the average number of side chain methyl radicals/molecule. While temperature alone may be an accurate means of fractionating these hydrocarbons to a level of constant molecular weight, it is noted that the value of D provides a more sensitive method and a better alternative.

For alkyl*cyclo*pentanes and alkyl*cyclo*hexanes the variation of D with (the number of side chains/total number of carbon atoms) is rather complicated; nevertheless, it has been possible to classify these hydrocarbons by their D values, on the basis of their ring content. By a method of trial and error, it was found that the relation of D and (the number of side chains/total number of carbon atoms) can be reduced to a straight line if D is plotted against $[D/(C_s/C_t) + a]$, where (Cs/Ct) is the ratio of the number of side carbon atoms to the total number of carbon atoms in the molecule. The parameter a was found to be nearly equal to unity. The formula representing the variation is

$$D = K\frac{[(C_s/C_t) + 1]}{[(C_s/C_t) + a - m]}$$

where K = intercept of the line (D *v.* $[D/(C_s/C_t) + 1]$),
m = slope of the line ($D_v \cdot [D/CC_s/C_t) + 1]$,
a = a parameter $\simeq 1$.

The plots of D versus $[D/(C_s/C_t) + 1]$ for alkyl*cyclo*pentanes and alkyl*cyclo*hexanes are shown in Fig 9.

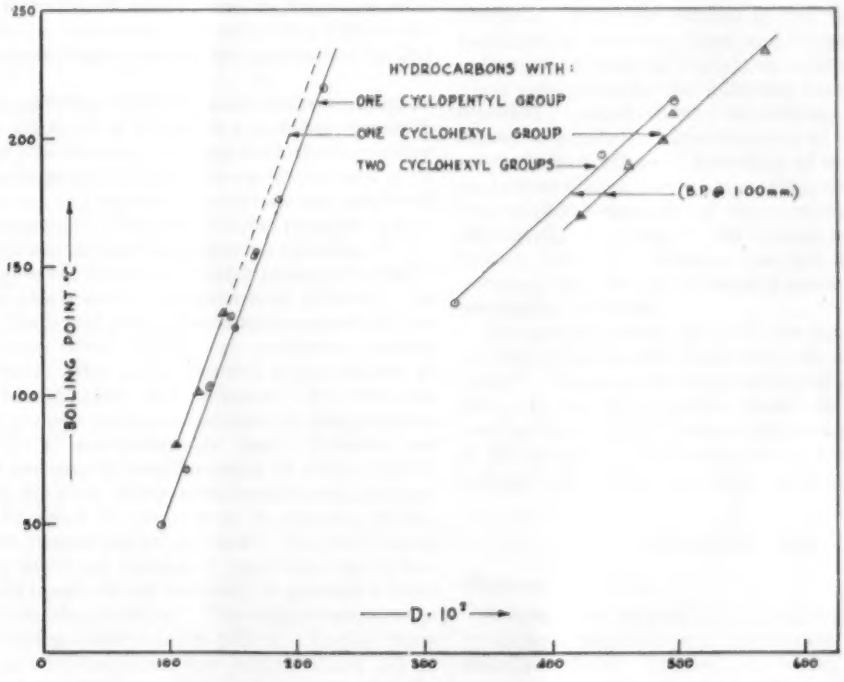


FIG 10

RELATION BETWEEN THE MAGNETO-OPTICAL ROTATION CONSTANT D AND BOILING POINT FOR ALKYL*CYCLO*PENTANES OR ALKYL*CYCLO*HEXANES

The broken line represents molecules containing three *cyclo*hexyl radicals for which sufficient data were not available. The values of K and m were estimated graphically. With $m = 2{\cdot}25$ and K having the following values :

Containing one *cyclo*pentyl group	−1·07
„ „ *cyclo*hexyl group	−1·33
„ two *cyclo*pentyl groups	−1·80
„ „ *cyclo*hexyl groups	−2·08

the equation is

$$D = K\,\frac{[(C_s/C_l) + 1]}{[(C_s/C_l) - 1{\cdot}25]}$$

The boiling point–D relationship of some naphthenes is illustrated in Fig 10. The lines are in two sections, one representing boiling points at 760 mm, and the other at 1·00 mm. In plotting D against the boiling point at 1·00 mm, it was assumed that the effect of pressure on boiling point is of the same extent for the various hydrocarbons concerned. Although the relationship is fundamental, it is of little value for mixture analysis.

In the above grouping of naphthenic hydrocarbons (Fig 10) it is noted that the classification is based on the ring content and also on the number of carbon atoms in the ring unit. Such classification can be used for the analysis of mixtures of each pair of groups, but the small differences in the properties of the various groups may limit the accuracy of the result.

References

[1] Waterman, H. I., Vlugter, J. C., and Van Westen, H. A. *J. Instn Petrol. Technol.*, 1932, **18**, 735; 1935, **21**, 661.
[2] Broersma, S., Waterman, H. I., Westerijk, J. B., and Wiersma, E. C. *Physica*, 1943, **10** (3), 97.
[3] Tadayon, J., Nissan, A. H., and Garner, F. H. *Analyt. Chem.*, 1949, **21**, 1932.
[4] Foehr, E. G., and Fenske, M. R. *Industr. Engng Chem.*, 1949, **21**, 1956.
[5] Westerdijk, J. B., Waterman, H. I., Span, H. F. O., Body, H., and Van New, K. *J. Inst. Petrol.*, 1950, **36**, 281.
[6] See Pt. I.
[7] Roberts, R. W. *Phil. Mag.*, 1931, **9**, 361; 1934, **17**, 934.
[8] Corbin, N., Alexander, M., and Egloff, G. *Industr. Engng Chem.*, 1947, **39**, 114–19.
[9] Smittenberg, J., and Mulder, D. *Rec. Trav. Chim.*, 1948, **67**, 813–25 (in English).
[10] Smittenberg, J., and Mulder, D. *Rec. Trav. Chim.*, 1948, **67**, 826–38 (in English).

POLYMERIZATION OF PROPENE WITH A SILICOTUNGSTIC ACID CATALYST*

PART I. BATCH EXPERIMENTS WITH UNSUPPORTED CATALYST

By J. J. VERSTAPPEN and H. I. WATERMAN

SUMMARY

Experiments on the polymerization of propene in the presence of silicotungstic acid as a catalyst are described; the present series is confined to batch experiments using catalyst without support.

Under standard conditions, conversions up to 86 per cent w could be obtained, the liquid polymer then containing 28 per cent w of tetramers. This indicates that silicotungstic acid is a more specific catalyst for tetramer production than phosphoric acid.

An insight into the structure of the dimers, trimers, and tetramers was obtained from physical and chemical data, including those provided by infra-red and mass spectrometry.

INTRODUCTION

THE tremendous increase in the use of surface-active agents during the last decade has led to a rise in the demand for C_9–C_{15} olefins. The polymerization of propene is a well-known process for the manufacture of olefins suitable for this purpose. Dimers and trimers of propene may also be used for blending with gasolines.

Although the literature describes the formation of tetramers from propene with numerous polymerization catalysts, including phosphoric acid, hydrogen fluoride, boron fluoride, aluminium chloride, etc., only phosphoric acid has found commercial application for this purpose.

With liquid orthophosphoric acid, the production on a commercial scale of polymers containing about 30 per cent of tetramers has been reported, the conversion of propene to polymers being about 86 per cent w on intake; a series of silver-lined reactors was employed for the conversion.[1] The use of liquid phosphoric acid on a quartz carrier has been reported elsewhere.[2]

For large-scale operation "solid phosphoric acid" catalyst is widely used in the petroleum industry. In this case, the liquid acid is, for instance, absorbed into diatomaceous earth (UOP) or activated carbon (I.G. Farben). The polymerization is carried out at elevated temperatures and pressures. For the conversion of propene to dimers and trimers, temperatures of 230°–250° C are commonly used. Trimers and tetramers are usually manufactured at about 205° C. In general, the yield of tetramers is relatively poor and amounts to about 13 per cent w on propene intake. The dimers formed can be recycled.[3] The injection of a carefully regulated amount of water into the hydrocarbon feed is sometimes necessary to prevent a rapid decrease in catalyst activity. Too high a water dosage causes softening of the catalyst pellets. In poly-plant practice this phenomenon has several times led to plugging of the reactor. Excellent reviews of polymerization with solid phosphoric acid catalyst have been published by Egloff, Weinert, and Sapper.[4]

In our attempts to develop a catalyst which would be more specifically suitable for the manufacture of propene tetramers and which could be used in the existing commercial poly-units, favourable results were obtained with several heteropoly-acids. These compounds may be regarded as formed by the union of a varying number of acid anhydride (oxide) molecules, especially of WO_3, MoO_3, and V_2O_5, with a second acid which furnishes the central atom of the polyanionic complex. Extensive studies in this field have been published by Souchay, Jean, and others.[5]

The use of heteropoly-acids as catalysts is not new. Their application for the following reactions has been reported: isomerization;[6] alkylation;[7] hydration of olefins to alcohols;[8] condensation of olefins with alcohols to form ethers;[9] formation of mono-carboxylic acids from olefins, carbon monoxide, and water;[10] or from aliphatic alcohols and carbon monoxide;[11] polymerization of styrene.[12] Of special interest in connexion with the investigations are two patents[13] covering the use of heteropoly-acids for the polymerization of olefins.

The present article discusses the polymerization of propene with the aid of silicotungstic acid catalyst as such.[14] Experiments were performed in batch operation. In the investigations described here, emphasis was laid on the performance and not on the structure of the catalyst. The evaluation of a continuous procedure with catalyst on a carrier is discussed in Part II.

EXPERIMENTAL

Propene Feed Stock

Propene was prepared on a semi-technical scale by continuous dehydration of *iso*propanol over activated alumina (Peter Spence) at about 330° C. The apparatus used has been described elsewhere.[15] The

* MS received 25 April 1955.

olefin was obtained in a purity of 99·9 per cent w, the remainder of the gas being hydrogen.

Catalyst Preparation

Silicotungstic acid was prepared by the following well-known procedure :[16]

Dissolve 1000 g of crystalline sodium tungstate in 2000 ml of water, add 75 g of water-glass (sp. gr. 1·375), heat to boiling and very slowly add 600 ml of hydrochloric acid (sp. gr. 1·18), while stirring vigorously. Cool to room temperature after filtering, add another 400-ml portion of hydrochloric acid and again cool. Shake with an excess of diethyl ether and isolate the lower layer formed. This is a complex of a heteropoly-acid and diethyl ether, which is decomposed by heating on a steam bath. The solid residue is again dissolved in 1000 ml of dilute hydrochloric acid (1 : 3). By shaking with an excess of diethyl ether, the oily complex is again formed. After heating this complex on a steam bath, dissolving the residue obtained in a small amount of water, and subsequently drying it, a procedure which is repeated several times, the silicotungstic acid can be obtained free from hydrochloric acid. The reaction taking place can be represented by the following equation :

$$12Na_2WO_4 + Na_2SiO_3 + 26HCl \longrightarrow (2H_2O.SiO_2.12WO_3). \times H_2O + 26NaCl + 11H_2O$$

In the experiments the catalyst was heated to constant weight at a temperature of 100° C or higher, as further described in the various experiments. Finally, the catalyst was powdered in a mortar.

POLYMERIZATION EXPERIMENTS

(a) *Reaction Conditions*

Batch experiments using catalysts with varying amounts of water of hydration were carried out at elevated temperatures and pressures, with for instance 200 g of propene in a 500-cc rotating autoclave. Autoclaves of stainless steel (Poldi-CV) were used.

The reaction begins at about 120° C, but is preferably carried out at a somewhat higher temperature, *e.g.* 150°–160° C.

In order to obtain a satisfactory reproducibility, it is necessary to dry the catalyst at temperatures between 160° and 300° C, as will be shown below. For the same reason careful drying of the propene is essential; the occurrence of traces of *iso*propanol is also harmful in this respect. The presence of hydrogen sulphide in the feed leads to the formation of addition compounds (mainly 2-propane-thiol and 2,4-dimethyl-3-thiapentane).

(b) *Influence of Catalyst Hydration on Activity*

The water content of the heteropoly-acid was found to play an important role in the batch experiments. A drying curve, obtained by heating the catalyst to constant weight at various temperatures and estimating the loss of water, is given in Fig 1. At about 160° C a certain amount of water is eliminated, owing to the transition of the 5-hydrate into the anhydrous silicotungstic acid ($H_4W_{12}SiO_{40} = 12WO_3.SiO_2.2H_2O$), which is stable over a wide temperature range. At about 440° C the heteropoly-acid decomposes into an intimate mixture of tungsten trioxide and silicon dioxide.

In the experiments with catalysts dried below 160° C, irreproducible results as regards conversion were often obtained, and aggregation of the catalyst occurred. The small amount of water escaping from the catalyst when the reaction temperature exceeds the catalyst drying temperature seems to be responsible for these phenomena. To obtain reproducible results it is necessary to use a catalyst dried between 160° C and about 300° C. Unless otherwise stated, all catalysts used in the experiments here described were dried at temperatures within these limits.

When the catalyst is dried above about 440° C prior to use, the resulting mixture of tungsten

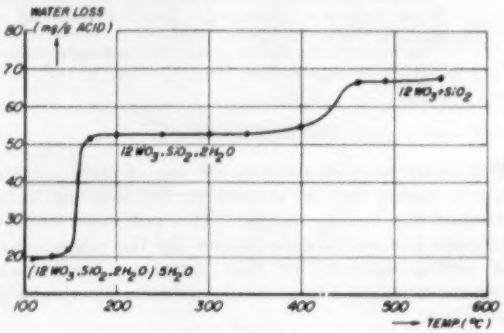


Fig 1

DEHYDRATION CURVE OF SILICOTUNGSTIC ACID

trioxide and silicon dioxide shows a much lower activity than the original silicotungstic acid. This is illustrated in Table I, which gives the results of polymerizations carried out with 180–200 g of propene and 10 g of catalyst in a 500-cc autoclave under the following conditions: reaction temperature 150°–160° C, heating-up period 15–20 minutes, reaction period 1 hr, rotation speed of the autoclave 24 r.p.m. After the reaction period the autoclave was cooled to room temperature as rapidly as possible with the aid of an air-blower.

Table I

Influence of Catalyst Drying Temperature on Activity

Catalyst drying temperature, ° C	Water content of catalyst, % w *	Conversion, % w
160	2·26	86
200	1·43	85
240	1·46	87
390	1·25	45
550	—	0

* Determined by heating to 500° C.

The mixture of WO_3 and SiO_2 may still be used as a polymerization catalyst if much higher reaction temperatures (*e.g.* about 350° C) are employed.

(c) *Product Yield Structure*

In all experiments a clear, light greenish-yellow liquid showing a green fluorescence was obtained. By

rectification a separation into various fractions was made. The boiling ranges of dimers, trimers, and tetramers were chosen so as to include the bulk of these polymers.

The influence of the catalyst drying temperature on the product yield structure is illustrated in Table II, which gives the results of a series of experiments carried out under the standardized conditions already mentioned in Section (*b*). It must be kept in mind

TABLE II

Influence of Catalyst Drying Temperature on Main Product Composition

Catalyst drying temperature, ° C	160–300	390	550
Reaction temperature, ° C	150–160	150–160	360–380
Conversion, % w on intake	86	45	69
Yield, % w on liquid product:			
Dimers (<80° C)	6	17	21
Trimers (125–150° C)	31	29	23
Tetramers (170–214° C)	28	19	18
Residue (>214° C)	28	25	26

that the polymerizations with catalysts dried at 550° C are not fully comparable with the other experiments, because higher reaction temperatures were necessary in the former case. They may provide useful information, however.

Conditioning of the catalyst at any temperature between 160° and 300° C does not affect the distribution of the main components of the product

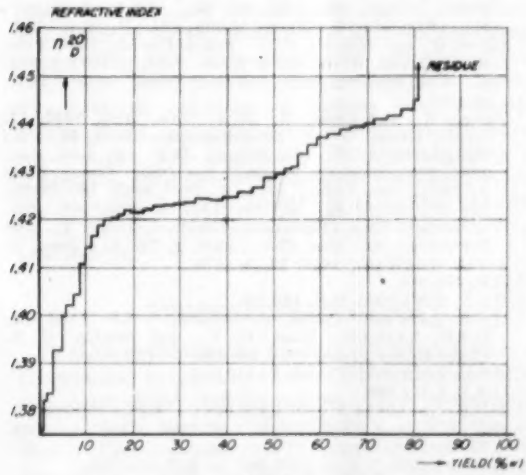


FIG 2

TYPICAL DISTILLATION CURVE FOR LIQUID POLYMERS

obtained. As will be seen from the results, drying within these temperature limits leads to the highest activity and to the greatest selectivity as regards tetramer formation.

Representative distillation curves for products obtained at reaction temperatures of 150°–160° C, when using 5 per cent w of silicotungstic acid (dried between 160° and 300° C) are given in Figs 2 and 3.

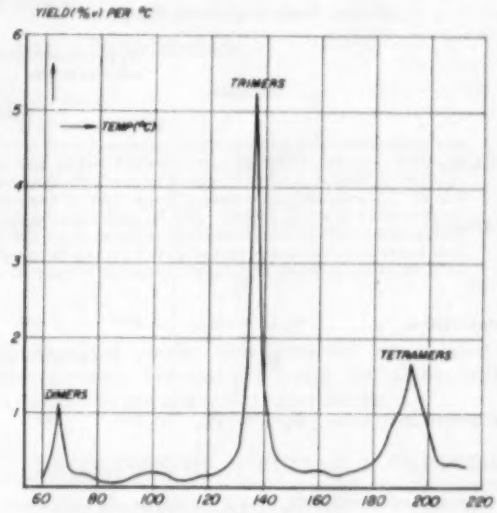


FIG 3

DISTRIBUTION OF POLYMERS IN REACTION PRODUCT

Some data for the main fractions from the same experiments are collected in Table III.

TABLE III

Properties of Propene Polymers

	Dimers		Trimers		Tetramers		Residue
Boiling range, ° C	53–71	75–125	125–150	150–170	170–190	190–214	
Refractive index, n_D^{20}	1·3955	1·4094	1·4246	1·4307	1·4362	1·4406	1·4595
Density, d_4^{20}	0·6839	0·7185	0·7447	0·7580	0·7709	0·7797	0·8200
Molecular weight	85	101	126	154	170	189	228
Olefins, % w	89 *	—	—	—	—	—	—
	85 †	—	—	—	—	—	—
H–C ratio ‡	—	—	2·041	—	1·999		

* Calculated from bromine number (156) by McIlhiney method.
† Ditto from "bromine number" (162) by ozonization.
‡ From elementary analysis.

(d) *Composition of the Polymer Product*

To gain some insight into the structure of the components in the reaction mixture, a dimer fraction (53°–71° C) was submitted to infra-red analysis. The result is given in Table IV. It must be kept in mind that *cis*-olefins and tetra-substituted olefins are not determined in this way. The amount of *cis*-olefins may be assumed to be of the same order of magnitude as the amount of *trans*-olefins.

A mass-spectrometric analysis (Table V) of a hydrogenated dimer fraction (54·4°–63·6° C) showed the presence of a considerable amount of 2-methylpentane. It appears that the amount of tetra-substituted olefins (2,3-dimethylbutene) in the dimer fraction prior to hydrogenation must be fairly small. In order to account for 85 per cent w olefins in the hexene fraction, the amount of tri-substituted olefins

must therefore be higher than 31 per cent w, as calculated from infra-red analysis.*

TABLE IV

Infra-red Analysis of Dimer Fraction

	Structure	Approximate concentration	
		Mol/litre	% w
α-Olefins	$C{=}C(H)-R_1$	0·2	2·5
α′-Olefins	$C{=}C(R_2)-R_1$	0·7	8·5
trans-Olefins	$R_2-C(H){=}C(H)-R_1$	0·7	8·5
Tri-substituted olefins	$R_1-C(R_2){=}C(H)-R_2$	2·5	31 *

TABLE V

Composition of Hydrogenated Dimers by Mass-spectrometric Analysis

2-Methylpentane	63 per cent v
3-Methylpentane	23 per cent v
2,3-Dimethylbutane	14 per cent v

An impression of the degree of branching of the trimers was obtained by infra-red analysis of the corresponding polymer fraction after hydrogenation (b.p. 127·6°–141·3° C after hydrogenation), see Table VI. The hydrogenations were carried out in a rotating autoclave at 200° C, with nickel on kieselguhr as a catalyst and at an initial hydrogen pressure of 125 atm.

TABLE VI

Infra-red Analysis of Hydrogenated Trimer Fraction

Group	Number of groups per mol	
	Determined (±0·4)	Calculated for *nn′*-dimethylheptanes and methylethylhexanes
CH_3	4·3	4
CH_2	2·7	3
CH	1·5	2

From the data given above it was concluded that the reaction product mainly consists of branched olefins. No straight chains are present. If it is assumed that no important skeletal rearrangement has taken place during hydrogenation, it is evident that the dimer fraction is composed to a major extent of 2-methylpentene-2, together with smaller quantities of 3-methylpentene-2, 4-methylpentene-2, and 2,3-dimethylbutene-2. In addition, 11 per cent w of α-olefins and 15 per cent w of saturates are present in the dimer fraction.

It seems unlikely that α-olefins or saturates are present in the trimer and tetramer fractions in any considerable amount. As regards the skeletal arrangement of the trimers, it may be concluded that these molecules contain only few quaternary carbon atoms and that the group analysis of this fraction indicates that the principal structures present are probably *nn′*-dimethylheptanes and/or methylethylhexanes.

The gas remaining after the experiments was found to be slightly less olefinic (95 per cent v) than the feed (98–100 per cent v); its composition was not further investigated.

From the presence of intermediate fractions in the distillation curves it is apparent that the reaction produces some hydrocarbons of which the number of carbon atoms is not a multiple of three. This leads to the conclusion that in addition to polymerization, isomerization, and hydrogen transfer, some disproportionation has also taken place.

The evaluation of a continuous procedure with the catalyst on a carrier is described in Part II.

References

1 Stüpel, H. "Synthetische Wasch- und Reinigungsmittel," p. 117. Stuttgart: 1954; FIAT final report 1141, pp. 75–7.

2 Langlois, G. E., and Walkey, J. E. *World Petrol. Congr.*, 1951, (4), 191. U.S.P. 2,579,433.

3 Ipatieff, V. N., and Pines, H. *J. Org. Chem.*, 1936, **1**, 473; Deeter, W. F. *Oil Gas J.*, 23.3.50, **48** (46), 252–8; Griesinger, W. K., and Hersberger, A. B. *World Petrol. Congr.*, 1951, (5), 87, 90; U.S.P. 2,500,307; B.P. 638,514; U.S.P. 2,486,533; U.S.P. 2,457,146.

4 Egloff, G., and Weinert, P. C. *Petrol. Process.*, 1948, **3** (6), 585; Sapper, W. *Erdöl u. Kohle*, 1951, **4**, 550; Egloff, G., and Weinert, P. C. *World Petrol. Congr.*, 1951, (4), 201.

5 Signer, R., and Gross, H. *Helv. Chim. Acta*, 1934, **17**, 1076; Kraus, O. *Z. Kristallographie*, 1935, **91**, 402; Illingworth, J. W., and Keggin, J. F. *J. chem. Soc.*, 1935, 575; Souchay, P. *Bull. Soc. Chim. France*, 1942, **9**, 289; *Ann Chim.*, 1942, **9**, 289; 1943, **18**, 61–95, 169–84; 1945, **20**, 73, 96; 1947, **2** (12), 203, 223; "Thesis," Paris, Sorbonne, 1945; Souchay, P., and Tchakirian, A. *Ann. Chim.*, 1946, **1**, 232–61; Jean, M. *Ann. de Chimie*, 1948, **12** (3), 470.

6 B.P. 496,676.

7 U.S.P. 2,301,966; B.P. 480,756.

8 U.S.P. 2,474,440; Canad. P. 390,498; U.S.P. 2,162,913; U.S.P. 2,173,187. Mace, C. V., and Bonilla, C. F. *Chem. Engng Progr.*, 1954, **50**, 385.

9 U.S.P. 2,018,065; French P. 710,846.

10 U.S.P. 1,924,766.

11 U.S.P. 1,940,987; U.S.P. 1,940,988; U.S.P. 1,940,989.

12 Day, J. H., and Solak, Th. A. *J. Amer. chem. Soc.*, 1951, **73**, 469.

13 B.P. 482,276; U.S.P. 2,301,966 (= B.P. 480,756).

14 Verstappen, J. J. "Katalytische polymerisatie van propeen, thesis." Holland: Delft Technological University, 1953.

15 Verstappen, J. J., and Waterman, H. I. *Ingenieur, 's Grav.*, 3.9.54, **66** (36), 77–9.

16 Marignac, M. C. *Ann. Chim. Phys.*, 1864, **3**, 1; Scroggie, A. C. *J. Amer. chem. Soc.*, 1929, **51**, 1057; Booth, H. S., "Inorganic Syntheses," Vol. I, 1st ed., p. 129. 1939.

* It may be remarked that owing to spectral phenomena the quantitative determination of tri-substituted olefins is not very accurate.

PART II. CONTINUOUS EXPERIMENTS WITH THE CATALYST ON CARRIER

By J. J. VERSTAPPEN and H. I. WATERMAN

SUMMARY

Further to the batch polymerizations of propene described in Part I, a series of continuous polymerizations was carried out. In this case, much proved to depend on a proper choice of the carrier for the catalyst. With 20 per cent w silicotungstic acid on bauxite favourable results were obtained in a semi-technical reactor-type polymerization unit. The technical propane–propene fraction used as feed stock contained approximately 50 per cent v of propene. A once-through operation in the temperature range of 150°–180° C, using pressures from 80 to 120 atm and space velocities between 0·22 and 0·54 USG/hr/lb catalyst, yielded liquid products containing 20–24 per cent w of tetramers. Under these conditions up to 95 per cent w of the propene was converted into liquid products. A preliminary life test of this catalyst on its carrier showed it capable of yielding up to 50 USG of polymer per lb.

INTRODUCTION

In Part I, a series of batch experiments with pure silicotungstic acid as polymerization catalyst and pure propene as feed was described. In view of the high tetramer yields obtained and the favourable activity of the catalyst, the performance of silicotungstic acid in continuous operation has now also been investigated. These experiments were carried out in a reactor-type polymerization unit. Preliminary experiments with the pure acid in pelleted form yielded intolerably large carbon deposits on the catalyst surface owing to the occurrence of high local temperatures. This phenomenon is undesirable, as it causes a considerable decrease of catalytic activity. The coke formation could be minimized satisfactorily by suitable choice of the carrier for the catalyst and by using a propane–propene fraction instead of pure propene as feed stock, the inert propane thus acting as a diluent. The catalytic activities of various catalyst–carrier combinations, as determined in small-scale batch experiments, are compared. Results obtained in continuous operation with the most promising carrier are discussed in more detail. It is realized that the use of various other carriers may also lead to favourable results.

PROPENE FEED STOCK

In these experiments a mixture consisting mainly of propene and propane was used. The propene content was about 50 per cent by volume. This mixture was produced in the catalytic cracking installation at Shell's Pernis refinery. It contained very small amounts of ethene, ethane, *iso*butane, and also 0·003 per cent w of mercaptans.

PREPARATION OF THE CATALYST ON CARRIER

The carrier materials were immersed in a solution of silicotungstic acid in water. After evaporation of the water at about 100° C with occasional stirring, the impregnated carrier thus obtained was heated at temperatures between 100° and 300° C as further indicated in the respective experiments.

SELECTION OF A SUITABLE CARRIER

Screening Experiments under Standard Conditions

For obtaining rapid information on the suitability of several carrier materials, a series of batch polymerizations, using various catalyst–carrier combinations, was carried out. In order to allow for a comparison of the conversion obtained, standard reaction conditions were carefully maintained in these experiments.

20 g of total catalyst on carrier containing 4 g of pure silicotungstic acid was heated with 40 g of carefully dried propene (purity 99·9 per cent w) at 150°–160° C in a 120-cm³ rotating autoclave for 1 hr (24 r.p.m.). The heating-up period amounted to 20–30 minutes, and the time necessary for cooling to room temperature was about 1 hr.

It is realized that these experiments give only indications of the initial activity of the catalyst, and that continuous operation with dried propene may exert some drying action on the catalysts, which may result in a change in activity.

The results of these experiments with various carriers are summarized in Table I.

Since diatomaceous earth is used as carrier in the UOP solid phosphoric acid catalyst, a study of its behaviour in combination with silicotungstic acid seemed interesting. The activity of this catalyst–carrier combination, however, was found to be very sensitive to variations in carrier quality, although very high conversions were obtained in several cases. Another disadvantage of diatomaceous earth is its poor tabletting property.

A sample of macroporous silica gel (as delivered by N.V. Droogtechniek, Rotterdam) also gave poor catalytic results.

Coke and various charcoals (not mentioned in Table I) proved to be somewhat indifferent carriers.

Several aluminas were tested with varying success. A remarkable fact is the influence which heat treat-

ment of this carrier in many cases has on the final activity of the catalyst prepared with it. In some cases, an increase of the heating temperature from 120° to 300° C, leading to only minor changes in water content or specific surface area, resulted in a considerable increase in the activity. An explanation for this phenomenon cannot be given. It is felt that the structure and the acidity of the alumina surface are of primary importance.

TABLE I

Experiments with 20 per cent w Silicotungstic Acid on Various Carriers

Carrier	Carrier			Catalyst on carrier	Conversion of propene to liquid products, % w (±2% w)
	Water * content, % w	Specific surface area, m^2/g †	Particle size	Temperature employed in preparation, ° C	
Diatomaceous earth (pure)	0·47	—	Powder	120	92
Diatomaceous earth (pure)	0·30	—	Powder	300	95
Diatomaceous earth (technical grade)	—	—	Powder	300	12
Coke ‡	—	—	5–10 mm	115	60
Coke ‡	—	—	5–10 mm	115	50
Coke §	1·53	—	5–10 mm	120	60
Silica gel	5·99	—	3–6 mm	120	12
Silica gel	5·81	—	3–6 mm	290	20
Pumice	5·56	—	4–7 mm	120	88
Bauxite	49·0	*ca* 2	5–8 mm	120	87
Bauxite	9·1	—	5–8 mm	300	97
Alumina (technical grade)	0·05	11	Powder	120	90
Alumina (Hopkin-Williams)	5·2	98	Powder	120	30
Alumina (Hopkin-Williams)	5·2	98	Powder	275	55
"Activated alumina" (Peter Spence)	27·7	90	5–10 mm	120	0
"Activated alumina" (Peter Spence)	25·0	90	5–10 mm	200	25
"Activated alumina" (Peter Spence)	18·0	90	5–10 mm	300	74
"Activated alumina" (Peter Spence) §	7·0	2	5–10 mm	120	42
Blank experiment. Catalyst 100% silicotungstic acid. No carrier	—	—	Powder	—	65

* At the drying temperature of the catalyst-carrier, based on the weight of the carrier after heating at 1000° C (for coke: 350° C).
† Calculated from lauric acid adsorption from pentane solution,[1] after drying the carrier at 300° C (bauxite: 120° C).
‡ Pretreated with 4N-HCl.
§ Carrier heated for 48 hr at 750°–800° C.

From the screening experiments it is concluded that, for the polymerization of propene, the suitability of a carrier for silicotungstic acid catalyst is largely determined by certain unknown properties and that a high specific surface area or high purity are not essential.

SCOUTING EXPERIMENTS WITH BAUXITE AND PUMICE CARRIER

Since the results obtained with bauxite and pumice were promising, a series of polymerizations was carried out with various concentrations of silicotungstic acid on each carrier. Except for the amount of catalyst, which was so chosen that the quantity of carrier was 16 g in all experiments, the standard conditions given for the first series of batch experiments were maintained. All catalysts were dried at 100°–110° C. The results are given in Table II. A striking result is that a suitable concentration of silicotungstic acid on either pumice or bauxite may yield a material with higher catalytic activity than that of the heteropoly-acid alone. In view of earlier results with inert carriers, it is felt that this effect cannot be ascribed to a better distribution of the heteropoly-acid, but must be owing to some interaction between the acid and the carrier. X-ray investigations carried out did not throw any light on this phenomenon. At low concentrations of heteropoly-acid the catalyst shows a higher activity on a bauxite than on a pumice base.

TABLE II

Comparison of Catalysts on Pumice and on Bauxite Basis

Concentration of silicotungstic acid on the carrier, % w	0	6	10	11	15	20		100
Conversion, % w:								
Bauxite basis	8	45	—	76	—	87	91 *	—
Pumice basis	—	16	29	58 *	—	80	88	86 * —
Non-supported catalyst	—	—	—	—	—	—	—	65

* Carrier pretreated with 4N-HCl

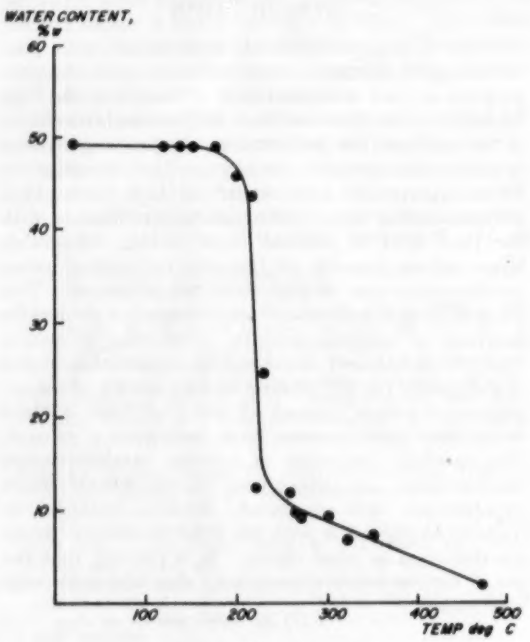


FIG 1
DRYING CURVE OF BAUXITE

The bauxite used was a white variety from Surinam. It consists mainly of the trihydrate of alumina, as was confirmed by X-ray analysis. It is assumed to have the structure of gibbsite. On heating above 190° C a considerable loss of water is observed (see Fig 1), whilst a transformation into other modifications of

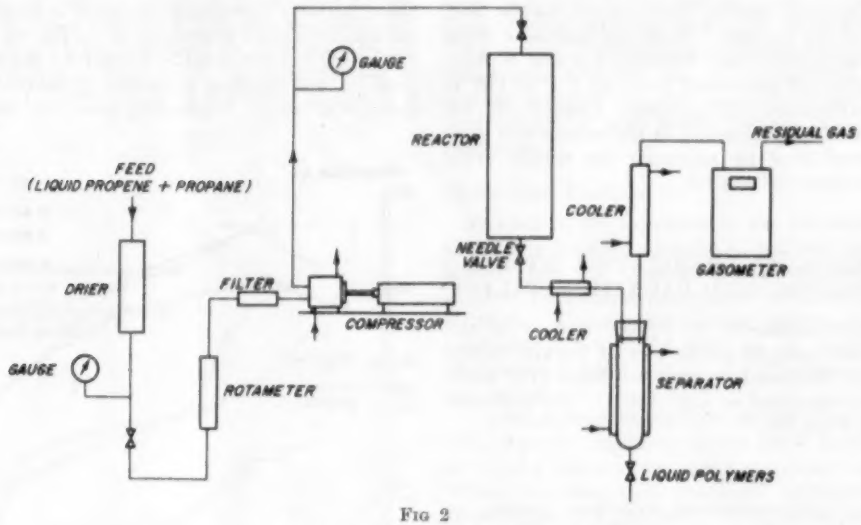


FIG 2
CONTINUOUS POLYMERIZATION UNIT
Polymerization of Propane with a Silicotungstic Acid Catalyst

alumina takes place. The activity of the catalyst on the carrier seemed to be unaffected by this structural rearrangement of the carrier, since equal conversions were realized in experiments with catalysts heated to 120°, 150°, 200°, and 260° C prior to use. Further experiments were carried out in continuous operation with bauxite as carrier material.

EQUIPMENT FOR CONTINUOUS POLYMERIZATION

A diagram of the unit is given in Fig 2. The liquid propene–propane mixture was dried with macroporous silica gel. Solid contaminants were removed by filtration through cotton-wool. By means of a plunger-type pump with adjustable stroke (capacity 0–1500 ml/hr) the liquid hydrocarbon mixture was pumped to the feed inlet at the top of the vertical reactor. The reaction products and the unreacted portion of the feed were withdrawn from the bottom of the reactor and cooled to 0° C. The liquid polymers were collected in a glass separator provided with a cooling jacket. Dissolved gases were removed in a distillation unit (not shown in Fig 1). Their volume was measured. The conversion was calculated from the amount of liquid polymers produced and the propene content of the residual gas, in order to eliminate uncertainties caused by slight variations in the pump stroke.

The stainless steel (Poldi-CV) reactor is shown in more detail in Fig 3. The catalyst bed was fixed between two layers of glass beads. Its top and bottom temperature could be measured with thermocouples. A practically constant temperature throughout the catalyst bed was maintained by a jacket around the reactor in which hot oil circulated. Owing to limitations of the available equipment, this jacket could be used only for temperatures below about 170° C.

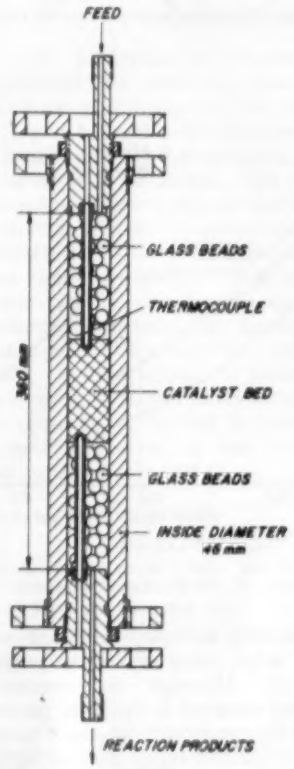


FIG 3
DETAILS OF REACTOR

Therefore, in the experiments at higher temperatures the reactor was provided with three electric furnaces,

allowing of separate heating of the upper, middle, and lower part of the reactor. With this heating system the temperature difference between top and bottom of the catalyst bed amounted to about 7° C at 175° C reactor temperature and a space velocity of 0·4 USG/hr/lb cat. The pressure in the reactor was kept at the desired level by adjusting the needle valve downstream from the reactor.

CONTINUOUS POLYMERIZATION WITH A SILICOTUNGSTIC ACID–BAUXITE CATALYST

The catalyst consisted of 20 per cent w of the heteropoly-acid and 80 per cent w of bauxite (white variety from Surinam) in granular form (3–7 mm). The catalyst was dried at 110°–120° C. Its apparent density was 2·9 g/m³.

Activity

A series of polymerizations with runs varying in length from 12 to 36 hr was carried out. For every run a fresh 150-g portion of catalyst was used, since it was found that interruption of the reaction caused considerable loss in catalytic activity. The relationships between conversion and space velocity at various pressure levels are shown in Figs 4 and 5 for 150°–160° C and 170°–180° C reactor temperatures respectively. The repeatability as regards conversion was ±1·5 per cent abs, when using separately prepared portions of catalyst. Although no decrease in catalytic activity was observed in the 36-hr period, it is stressed that the figures given relate only to fresh catalyst. The space velocity range covered includes the value normally applied in the UOP process (0·25 gal/hr/lb cat) for gasoline manufacture. The lower activity sometimes observed at small values of the space velocity is thought to be due to insufficient " washing " of the catalyst surface by the dense phase present. In the first moments of operation a small amount of water, originating from the catalyst, was observed in the liquid reaction products. This dehydration did not affect the catalyst performance, nor were phenomena due to plugging induced. If desired, the separation of water can be avoided, however, by drying the catalyst prior to use at temperatures slightly higher than the reaction temperature.

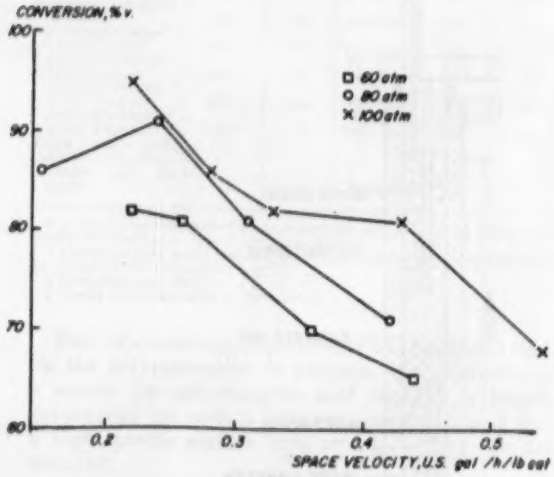


FIG 4

POLYMERIZATION AT 150°–160° C WITH 20 PER CENT SILICOTUNGSTIC ACID ON BAUXITE CARRIER

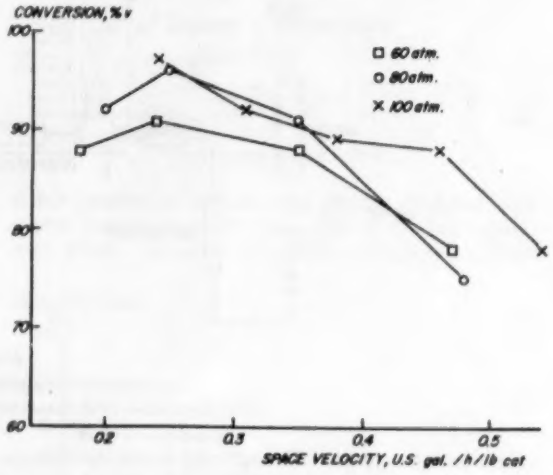


FIG 5

POLYMERIZATION AT 170°–180° C WITH 20 PER CENT SILICOTUNGSTIC ACID ON BAUXITE CARRIER

Selectivity

Tables III and IV present data on the composition of the liquid products obtained. In spite of shorter contact times in comparison with batch experiments reported earlier,[3] the percentage of tetramers in the liquid reaction products was still as high as 20–24 per cent w. Preliminary experiments showed that recycling of dimers and trimers will further increase the production of tetramer. Fig 6 shows that the silicotungstic acid catalyst is considerably more selective for the preparation of propene tetramers than the UOP type 1 solid phosphoric acid catalyst. Less disproportionation to products with 7, 8, 10, etc., carbon atoms occurred.

TABLE III

Composition of Polymer

	Hexenes		Nonenes		Dodecenes	
Boiling range, ° C .	50–80	80–125	125–150	150–170	170–214	Residue
Yield, % v . .	6–14	5–10	24–37	3–5	20–24	9–27

The F2 and F1 octane numbers, determined for the 60°–170° C fraction were 77·3 and 93·8 respectively. If these data are compared with those usually found for propene polymers obtained in the UOP process, it appears that the F2 octane of the latter is nearly 4 units higher.

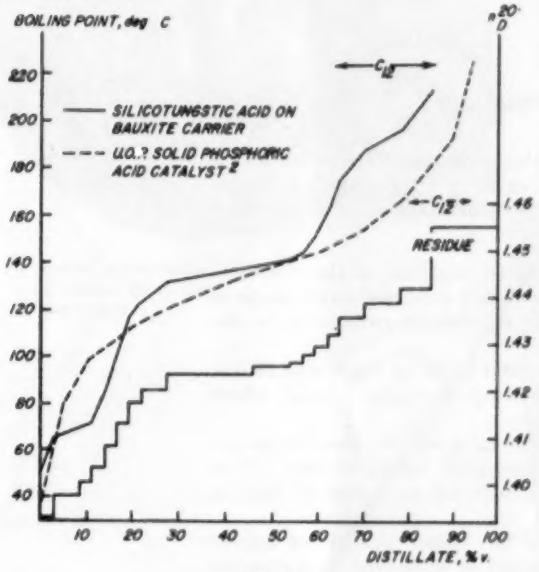


FIG 6

DISTILLATION CURVES OF PROPENE POLYMERS

TABLE IV

Influence of Reaction Conditions on Tetramer Yield

Reaction temperature, °C	Pressure, atm	Space velocity, USG/hr/lb cat	Tetramer (170°–214° C) yield, % v
150–160	60	0·22	23
	60	0·44	21
	100	0·22	24
	100	0·54	20
170–180	60	0·18	23
	60	0·47	20
	100	0·46	20
	100	0·54	20

Life

In a preliminary life test, in which the temperature was increased from 150° to 250° C, the catalyst proved capable of producing 50 USG of polymer/lb catalyst. The experiment was stopped when the conversion dropped below 50 per cent. It is believed that the actual producing capacity of the catalyst is much higher than the value mentioned above, as the reaction conditions employed were not optimal. Since the price of silicotungstic acid is relatively high, regeneration of the catalyst may be necessary for economic reasons. All regeneration procedures requiring temperatures above about 450° C are ruled out, since the heteropoly-acid begins to decompose at about 450° C. Conventional burning with inert gases containing a few per cent of free oxygen is therefore unsuitable. It was found, however, that if the amount of carbonaceous deposits on the catalyst is not too high, extraction (*e.g.* with diethyl ether) can be used for regeneration.

Operational Features

In none of the experiments was phenomena due to plugging observed, not even at reaction temperatures higher than the catalyst drying temperature. The catalyst on bauxite has a quite satisfactory crushing strength. The solubility of the catalyst in the liquid products is low: the amount of catalyst in the distillation residue (b.p. > 214° C) was less than 0·01 per cent w.

Corrosion tests carried out at 100° C with a 4·5 per cent aqueous solution of the pure heteropoly-acid revealed a distinct corrosion towards low carbon steel, whilst stainless steel remained unattacked. With suspensions (1·5 per cent w) of the crystalline acid (5 aq) in kerosine neither of these materials was corroded under similar conditions. Furthermore, no corrosion was observed in the Poldi CV reactor after prolonged use for continuous polymerization.

CONCLUSIONS

For the production of propene tetramers, silicotungstic acid on a carrier (*e.g.* bauxite) appears to have advantages in comparison with the UOP solid phosphoric acid catalyst. No injection of water with the feed is necessary, so that plugging of the catalyst bed is reduced to a minimum. The reactor temperature is considerably lower than in the UOP process, which also tends to minimize plugging, since less carbonaceous material is deposited on the catalyst surface. Because of the higher specific gravity of the catalyst, smaller reactors can be used for the same production. In once-through operation the tetramer content of the reaction product is nearly twice as high as in the UOP process. A disadvantage of silicotungstic acid is its higher price. Further experiments on a pilot plant scale must be performed in order to allow for an economic evaluation of this and related catalysts based on heteropoly-acid.

ACKNOWLEDGMENTS

Thanks are due to Ir J. W. Klinkenberg for doing part of the experimental work. Advice and assistance were received from the Koninklijke/Shell-Laboratorium, Amsterdam.

References

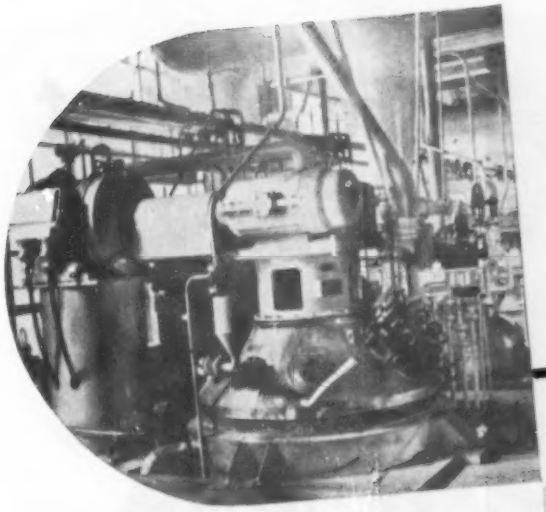
[1] Houben, G. M. M. Thesis, Delft Technological University, Institute of Chemical Engineering, 1951.

[2] Egloff, G., and Weinert, P. C. *World Petrol. Congr.*, 1951, (4), 201.
Deeter, W. F. *Oil Gas J.*, 23.3.50, **48** (46), 252–8.

STUDENT'S PRIZE

THE Council of the Institute of Petroleum has decided to award annually a Student's Prize to the value of £10 for the best paper submitted by a student during the year. The conditions under which the award will be made are :

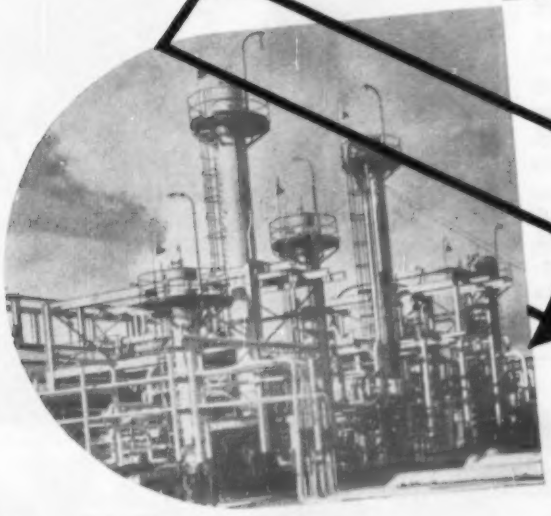
1. Candidates should be student members of the Institute, and the subject of their papers should come within the scope of the Institute's activities and be suitable for publication by the Institute.
2. Papers should not exceed 5000 words in length and should be accompanied by line drawings or photographs where necessary.
3. Papers should preferably be in typescript (two copies are desirable), but may be in manuscript if legibly written. They should be submitted to the Institute not later than 30 April in any year.
4. The name and address of the author should not appear anywhere on the paper, but should be submitted on a separate sheet of paper.
5. The first award will be made in 1956, but the Institute reserves the right to withhold the prize in that or any other year in which no paper is considered to merit an award. The decision of the Council of the Institute is final.



Grease Manufacturing Plant
(a Vacuum Oil Co. Ltd. photograph).

For special processes, anywhere, on any scale...

Autofining (Catalytic desulphurisation) Plant
(a B.P. Ltd. photograph).



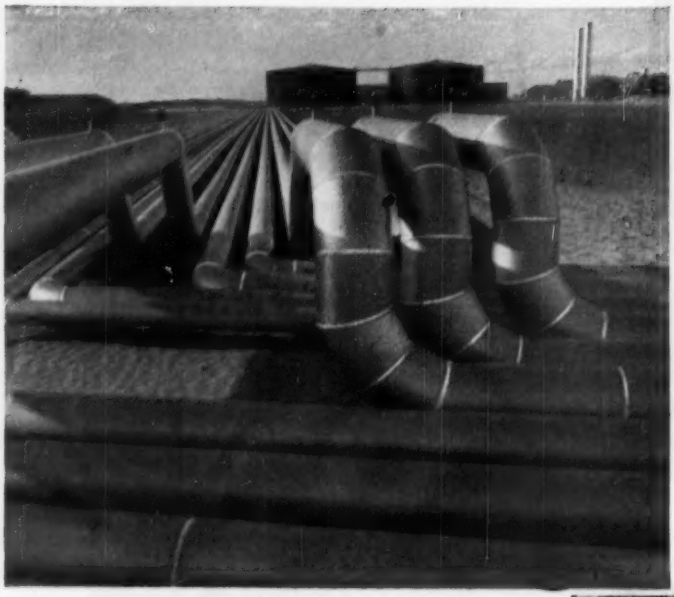
Petroleum Chemical Plant
(a Shell photograph).

consult—

W. J. FRASER & CO. LTD.

W. J. FRASER & CO. LTD., HAROLD HILL, ROMFORD, ESSEX. *Works: Monk Bretton, Barnsley, Yorkshire*

TAS. PS.443



The biggest refinery in Australia

FLEETWELDED BY LINCOLN

TWO YEARS AGO a few men and machines began clearing a scrub-covered, sandy area 12 miles from Freemantle, Western Australia. Today the 900 acre site is alive with activity. Three thousand men have just completed the gigantic £30 million Kwinana Refinery which will have a throughput of 3 million tons of oil a year.

The contractors, Kwinana Construction Group (Pty) Ltd., for the Australasian Petroleum Refinery Ltd. (the Australian associate of the British Petroleum Company Ltd.) specified that only Lincoln Fleetweld 5 Electrodes and Lincoln diesel welding machines must be used for all the vital parts of this vast project. Four sections of a high-fractioning tower 127 feet high and weighing 55 tons were Fleetwelded on site, the welds being inspected by X-Rays and Gamma Rays.

Three thousand miles of piping from $\frac{1}{4}''$ to 5′ in diameter and two pipelines 6″ and 12″ diameter were Lincoln welded. Many of the vertical piles for the jetty at Cockburn Sound are over 100 feet in length and were shipped in two parts, before being welded on site.

For all this exacting work, many welding operators of Kwinana Construction Group (Pty) Ltd. were trained in the Lincoln Welding School and used Lincoln Fleetweld 5 Electrodes and Lincoln S.A.E. Diesel Welders exclusively on this major project.

Lincoln Fleetweld 5 is used universally on pipe lines and during construction stages of all modern refineries for the Oil Industry.

Photo by kind permission of B.P.C.

LINCOLN

Largest manufacturers of D.C. Welders in the United Kingdom

LINCOLN ELECTRIC CO LTD · WELWYN GARDEN CITY · HERTS · WELWYN GARDEN 920

SM90

ON A SUNNY MORNING in 1952 nine men walk to work. They are Australians walking into the biggest thing their country has seen for years, a 3-year epic that will change a desolate area of scrub and sand into the Continent's largest, most important oil refinery: Kwinana!

Kwinana, on the shores of Cockburn Sound, 12 miles from Fremantle, was completed months ahead of schedule! Now, this £A40,000,000 project can handle 3 million tons of Middle East crude a year, possesses its own oil port, and a jetty which is large enough to take three tankers at a time.

Here is the familiar 20th Century skyline: slim, steel towers, bulbous spherical storage tanks, the huge tower of the catalytic cracking plant dominating a landscape where miles of piping stretch across the sand.

And for the men who work at Kwinana there is a township to settle in, to bring up their families in. History is being made, a future is being born.

Behind the achievement is the Kwinana Construction Group (Pty.) Ltd. This consortium of three British companies was formed to build the entire plant for Australasian Petroleum Company (an associate of the British Petroleum Co. Ltd.) to the designs of M. W. Kellogg Co. and the Kellogg International Corporation. So successful has this consortium been that the association will continue to build and to design similar installations throughout the world.

A Key to Australia's tomorrow

The Kwinana Construction Group(Pty) Ltd.

LONDON OFFICE 54 VICTORIA STREET, LONDON, S.W.1 *TATe Gallery 0683*

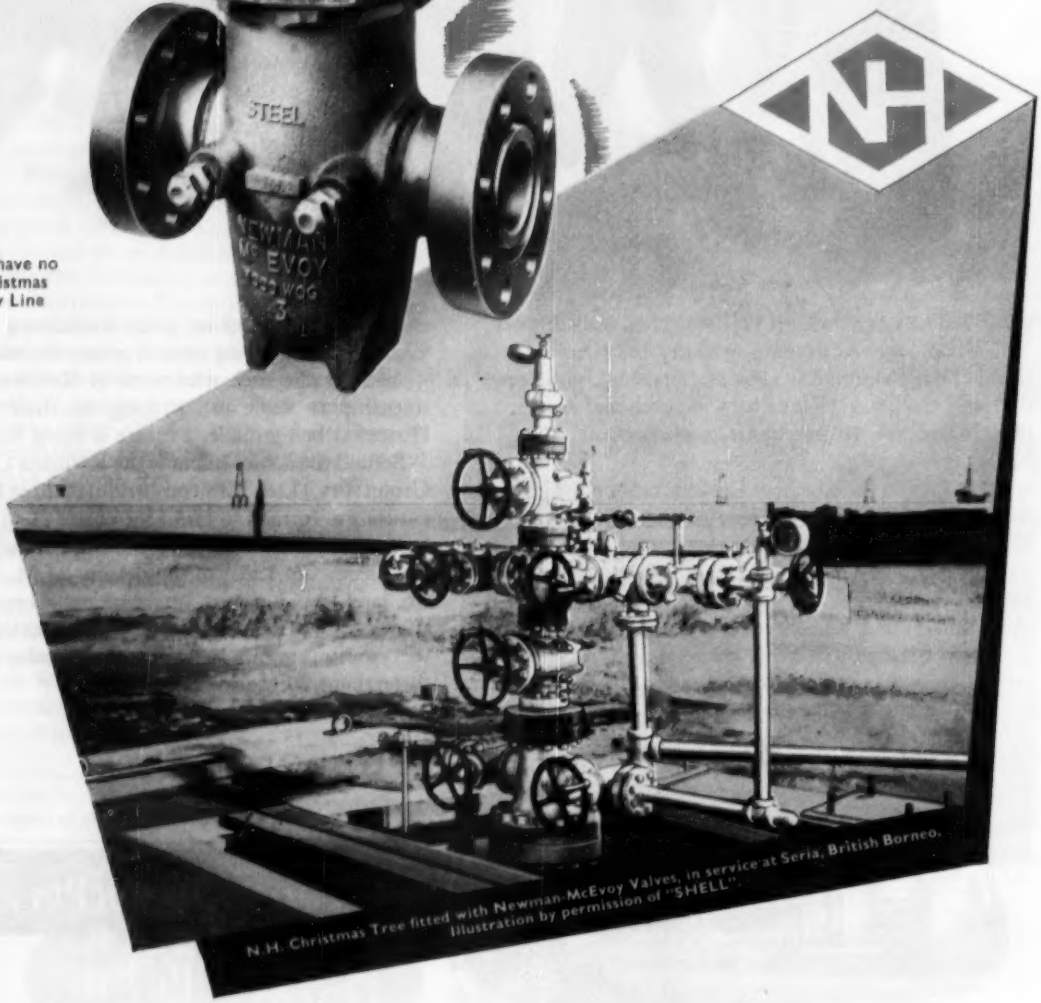
TA 5442

NEWMAN-McEVOY VALVES

These Valves have no equal for Christmas Tree and Flow Line service.

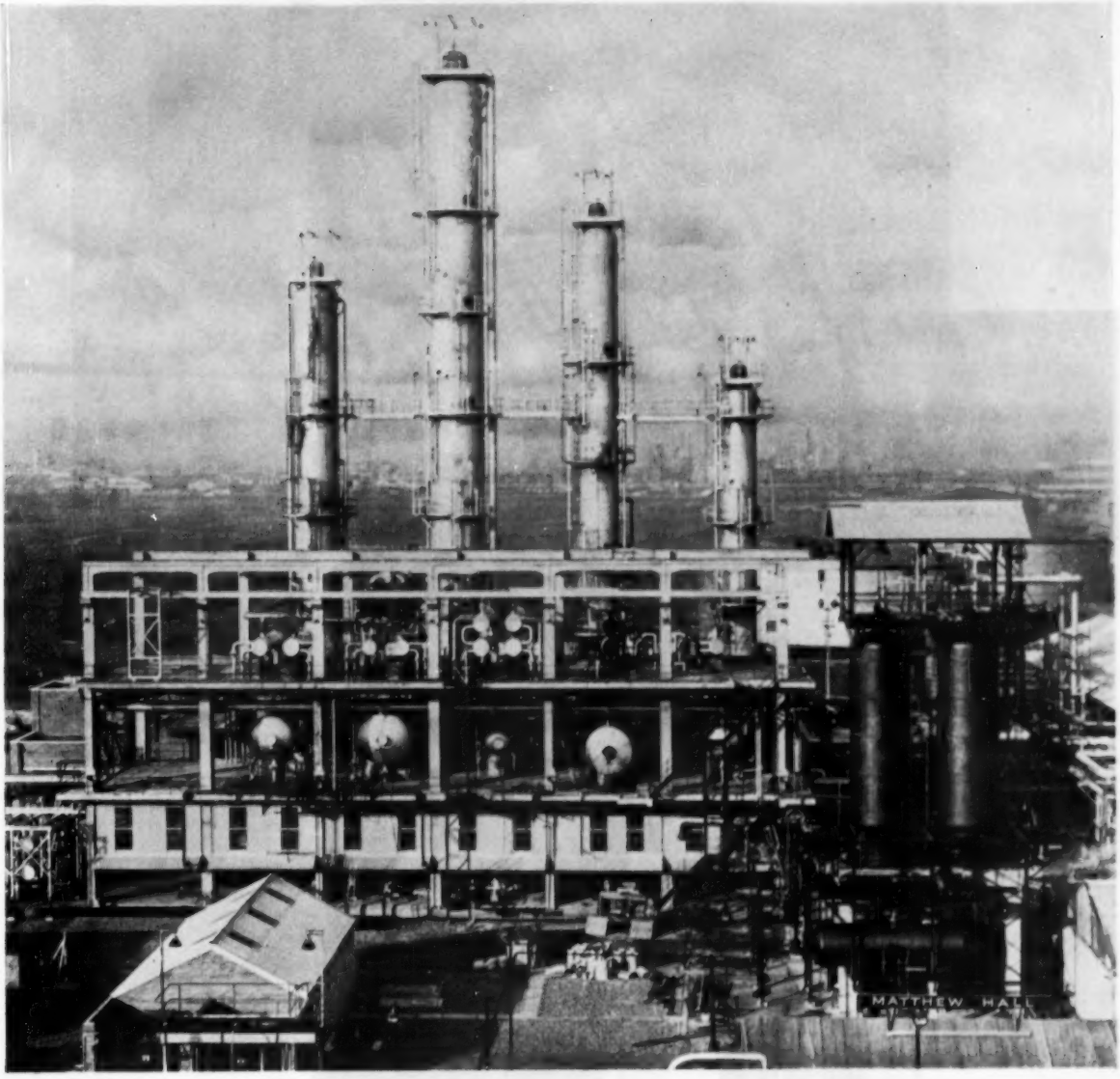
AUTOMATIC SELF-SEALING CONDUIT GATE VALVES

Newman–McEvoy Valves are available with Screwed, Socket Weld or Flanged Ends (illustrated). Valves for 1,000 lb., 2,000 lb., 3,000 lb., 5,000 lb., and 10,000 lb. W.O.G. pressures are manufactured in 2", 2½", 3", and 4" sizes. Write for illustrated and descriptive brochure.



N.H. Christmas Tree fitted with Newman-McEvoy Valves, in service at Seria, British Borneo. Illustration by permission of "SHELL".

Newman, Hender & Co. Ltd. WOODCHESTER STROUD GLOS.



THE

MATTHEW HALL

GROUP OF COMPANIES

OIL REFINERY ENGINEERS

ESTD. 1848

MATTHEW HALL

MATTHEW HALL HOUSE, DORSET SQUARE, LONDON, N.W.1

Glasgow Manchester Bristol Belfast Dublin Johannesburg Germiston Durban
Cape Town Welkom Lagos Bulawayo Salisbury (Central Africa) West Indies

WHESSOE

S&J

GAUGES

THE INTERNATIONAL STANDARD

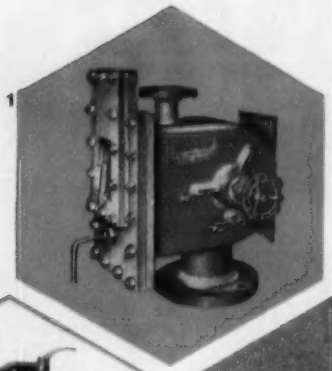
Manufactured by Whessoe under licence from the Shand and Jurs Company, California, the S & J gauging equipment has a world-wide reputation for accuracy and reliability.

The range includes gauge hatches, 'tell-tale' gauges, semi- and fully-automatic tank gauges for fixed and floating roof tanks and for high pressure storage spheres.

All S & J automatic gauges can be equipped with remote reading equipment enabling the gauges to be read with great accuracy several miles away.

Illustrated are (1) ST-400 high-pressure automatic tank gauge (versions available for pressures up to 450 p.s.i.g.), (2) ST-6500 combination gauge hatch and vapour line shut-off, (3) ST-2250 pressure type gauge hatch, (4) ST-5340 semi-automatic gauge and sampling lock (for pressures up to 10 p.s.i.g.), (5) ST-2935 automatic tank gauge.

Write for catalogue describing the Whessoe range of S & J fittings.

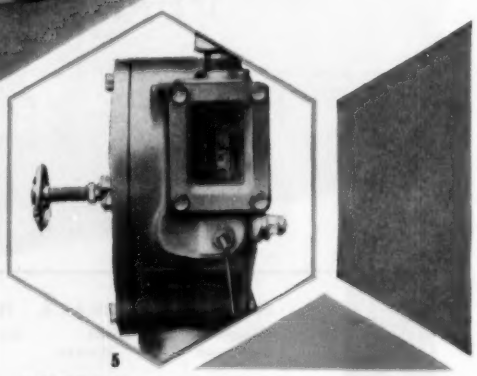


1

2

3

4



5

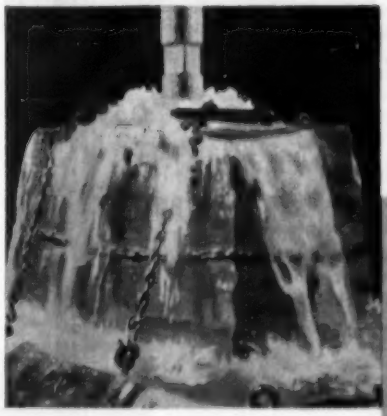
WHESSOE LIMITED DARLINGTON & LONDON

Telephone: Darlington 5315 · London Office: 25 Victoria Street, London, S.W.1 · Telephone: Abbey 3881

W75

We drill dry holes . . . on purpose

We drill our "dry holes"—hundreds per year—in the research laboratory . . . and they *produce* better rock bits . . . bits that enable you to drill wells faster and more economically. We drill these "dry holes" to test bit designs and materials under simulated field conditions. Facts learned from these HUGHES tests have helped to produce bits that are saving days in drilling wells and have made it possible to drill areas that otherwise would not have been drilled. Our "dry holes" have played an important part in aiding the producing industry to add billions of barrels to the oil reserves.



HUGHES
TOOL COMPANY
HOUSTON, TEXAS
WORLD STANDARD OF THE INDUSTRY

BRITISH SUBSIDIARY: HUGHES TOOL COMPANY, LIMITED—LONDON, ENGLAND
BARCLAYS BANK BUILDING, 73 CHEAPSIDE, LONDON, E. C. 2, ENGLAND

BROTHERHOOD

STEAM TURBINES

FOR DRIVING PUMPS, ETC.

Wide range—All types.
Over 40 years' experience.
Hundreds in hand—thousands in service.

BROTHERHOOD

STEAM ENGINES

High Speed Vertical up to 500 B.H.P.
Many in hand and hundreds in service.

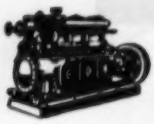
BROTHERHOOD

COMPRESSORS

Air, Gas and Refrigerating.
The widest range in the British Empire—made to suit your requirements.
Thousands in service.

BROTHERHOOD

REFRIGERATING PLANT



Ammonia, CO_2, Freon, SO_2, Methyl Chloride. Wide range—single and double acting—one or more stages.
Made to measure for special duties.

BROTHERHOOD

GENERATING SETS

Turbine driven up to 11,000 kw.
Engine driven up to 340 kw.
Scores in hand, hundreds in service.

also Manufacturers of all kinds of
PLANT TO CUSTOMERS' OWN DESIGNS

WHY NOT SEND YOUR PROBLEMS TO US?

We shall be pleased to investigate them confidentially without commitment

PETER BROTHERHOOD
PETERBOROUGH ENGLAND
COMPRESSION & POWER PLANT SPECIALISTS FOR NEARLY A CENTURY

CECA

CLARSOL:
DRILLING BENTONITES

CLARSIL:
ACTIVATED EARTHS

CLARCEL:
FILTER AIDS

ACTICARBONE:
ACTIVATED CARBONS

THE BRITISH CECA COMPANY LTD.
175 PICCADILLY, LONDON, W.1

Telephone: **HYDE PARK 5131-5**
Cables: **ACTICARBON, LONDON**

ADVERTISERS

Babcock & Wilcox Ltd.	Oct
Bailey Bros. & Swinfen Ltd.	Jan
Baker Oil Tools Inc.	Oct
Birmingham Battery & Metal Co. Ltd.	Oct
British Ceca Co. Ltd.	viii
Peter Brotherhood Ltd.	viii
W. P. Butterfield Ltd.	xiv
Chemindex Ltd.	Apr
Compoflex Ltd.	ix
Connaught Rooms Ltd., The	July
A. F. Craig & Co. Ltd.	xii
Dorman & Smith Ltd.	Apr
Electroflo Meters Co. Ltd.	Mar
English Drilling Equipment Co. Ltd.	Mar
Evershed & Vignoles Ltd.	Mar
Foster Wheeler Ltd.	Oct
Foxboro-Yoxall Ltd.	Sept
W. J. Fraser & Co. Ltd.	i
General Refractories Ltd.	Oct
Matthew Hall & Co. Ltd.	v
Hayward-Tyler & Co. Ltd.	July
Hughes Tool Co.	vii
Hydronyl Syndicate Ltd., The	Oct
Imperial Chemical Industries Ltd. (Metals Division)	xvi
India Rubber, Gutta Percha & Telegraph Works Co. Ltd., The	Sept
Kellogg International Corporation	Oct
Wm. Kenyon & Sons Ltd.	xv
Richard Klinger Ltd.	Oct
Kwinana Construction Group (Pty) Ltd., The	iii
Lake & Elliot Ltd.	Oct
Lincoln Electric Co. Ltd.	ii
A. & J. Main & Co. Ltd.	xiii
Mervyn Instruments Ltd.	Oct
Metal Propellers Ltd.	Oct
Metropolitan-Vickers Electrical Co. Ltd.	Sept
L. A. Mitchell Ltd.	Mar
A. P. Newall & Co. Ltd.	Sept
Newman, Hender & Co. Ltd.	iv
Oil and Petroleum Year-Book	x
Oxford University Press Ltd.	July
Power-Gas Corporation Ltd., The	Oct
Procon (Gt. Britain) Ltd.	Oct
Rubery, Owen & Co. Ltd.	Sept
South Durham Steel and Iron Co. Ltd.	Oct
Sunvic Controls Ltd.	Oct
Universal Oil Products Co.	xi
G. & J. Weir Ltd.	Oct
Whessoe Ltd.	vi
Henry Wiggin & Co. Ltd.	Oct
Woodfield Hoist and Associated Industries Ltd.	Jan
Yorkshire Copper Works Ltd., The	xiii

The lightest reinforced hoses on the market–

COMPOFLEX FEATHERWEIGHT

For extreme lightness and ease of handling there's nothing to compare with this all-purpose flexible which is one of a new range of suction and delivery hoses based on Compoflex principles. New combinations of synthetic materials have been used for the walls, together with an entirely new method of bonding and curing by heat treatment.

As a result, the FEATHERWEIGHT combines unusual lightness, great strength and flexibility, with improved durability and crush-resistance. It can also handle a wider variety of chemicals, including pure Benzoles, petroleum and oils, and is the ideal hose for road, rail and similar tank haulage work.

The FEATHERWEIGHT, which costs the same as the well-known standard OILMASTER, can be supplied in lengths up to 30 ft. with 1-in. to 4-in. bores. Alternative linings can be supplied at extra cost for special purposes.

For corrosive and abrasive conditions. Two new SMOOTH BORE hoses are available. The FLOWMASTER has a completely embedded spiral so that the metal cannot be attacked by the flowant. In the BANTAM, the spiral is flush with the inner surface, giving the lightest possible smooth bore hose.

For extra-heavy duty. Still stronger and tougher but lightweight Bargemaster and Jettymaster hoses are recommended for barge, ocean terminal and similar work. (6" and 8" bores).

TANK HAULAGE OPERATORS SAY:–

- ☆ IT'S HALF THE WEIGHT OF ANY OTHER HOSE
- ☆ IT'S EASY TO HANDLE
- ☆ IT'S TOUGH AND FLEXIBLE

If you have a ' flexible ' problem, you'll find the answer at Compoflex

Typical Weights and Working Pressures

I.d.	Weight per foot	Bend Radius	Working Pressure
Inches	Lbs.	Inches	Lbs. P.S.I.
2"	·9	3½"	200
2½"	1·37	5½"	175
3"	1·6	6"	175

THE FEATHERWEIGHT

Produced by **COMPOFLEX**

Sales Advisory Service at 52 Grosvenor Gardens, London, S.W.1. Tel: SLoane 0155/6/7 & Huddersfield Road, Oldham. Tel: Main 6114

NOW READY

Published October 1955 *Forty-sixth Year*

OIL & PETROLEUM YEAR BOOK 1955

Compiler: WALTER E. SKINNER

Price Thirty Shillings Net

Post Free (Inland and Abroad), Thirty-one shillings and sixpence

700 pages In Demy 8vo, bound in RED cloth

THE STANDARD REFERENCE BOOK
OF WORLD OIL COMPANIES

970 COMPANIES

The book is invaluable to everybody interested in this important industry, its contents comprising complete and up-to-date particulars concerning companies operating in all branches, Producers, Refiners, Transporters and Dealers. Arranged in alphabetical order.

BOOK CONTAINS INFORMATION ON THE PRINCIPAL
BRITISH, AMERICAN, CANADIAN AND
FOREIGN COMPANIES

Particulars given of each Company includes the Directors and other officials; date of incorporation; seat of operations; nature of business, description of property, refining and other plant, crude oil production; refinery runs; details of capital; dividends paid; and the financial position as disclosed by the latest accounts. Highest and lowest prices of the shares for the last three years.

MANAGERS, ENGINEERS, AGENTS, etc. 663 names and addresses and the names of the companies in the book with which they are connected.

BUYERS' GUIDE: A List of Manufacturers of Oilfield and Refinery Equipment and Accessories comprising 883 headings.

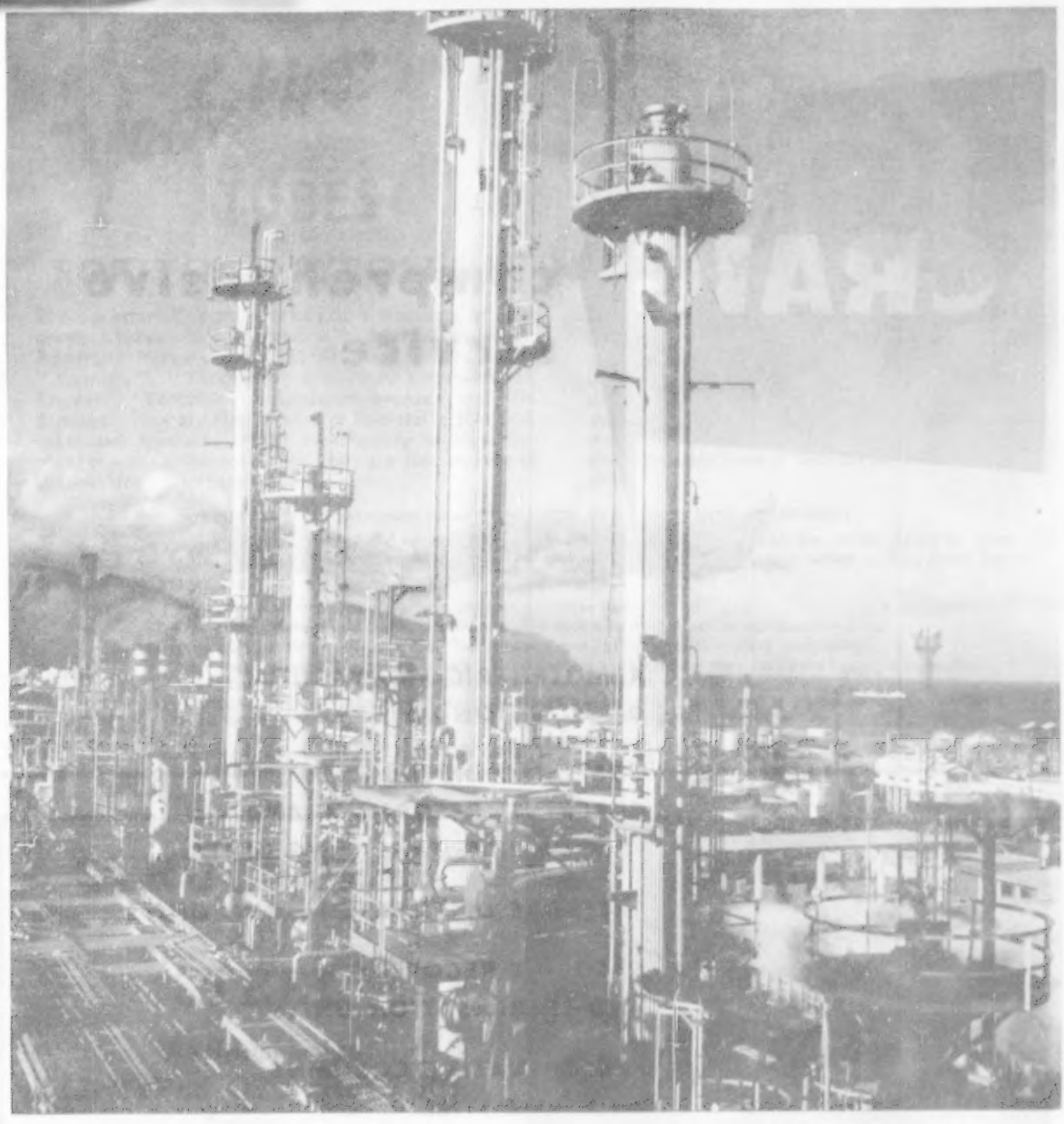
Advertisements: 300 Firms connected with the Oil Industry advertise in the book.

Obtainable from all Booksellers, or direct from the Publisher—

WALTER E. SKINNER

20 COPTHALL AVENUE, LONDON, E.C.2

Telephones: NATIONAL 8550 and 9920



Among the many licensees of the

UOP PLATFORMING PROCESS

is C. E. P. S. A.—Santa Cruz de Tenerife (Spain)
with a 5,000 barrel per stream day unit.

UNIVERSAL OIL PRODUCTS COMPANY

30 ALGONQUIN ROAD, DES PLAINES, ILL., U.S.A.
REPRESENTATIVE IN ENGLAND: F. A. TRIM,
BUSH HOUSE, ALDWYCH,
LONDON, W. C. 2

Universal Service Protects Your Investment

comprehensive service

ATMOSPHERIC AND VACUUM DISTILLATION UNITS

COMBINED DISTILLATION, CRACKING, REFORMING AND VAPOUR PHASE TREATING UNITS

PRESSURE DISTILLATE RE-RUN UNITS

GASOLINE RECOVERY AND STABILISATION UNITS

FRACTIONATING COLUMNS AND TUBE STILLS

WAX REFINING, SWEATING AND MOULDING

A. F. Craig & Company Limited

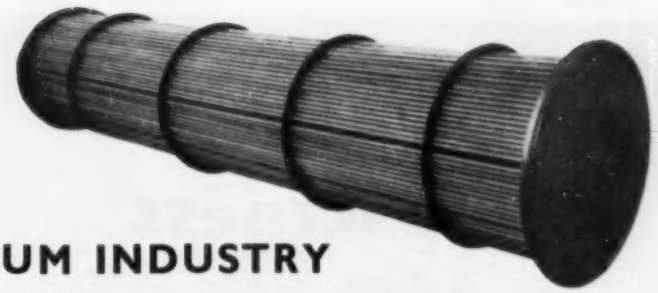
Caledonia Engineering Works

Paisley, Scotland

London Office: 727 Salisbury House, London Wall, E.C.2. Phone: NATional 3964

C11

"Yorkshire" TUBES



FOR THE PETROLEUM INDUSTRY

The Yorkshire Copper Works Ltd. are makers of solid drawn tubes in "Yorcalbro" (aluminium-brass), Admiralty Mixture Brass, 70/30 Brass, "Yorcoron", "Yorcunic", "Yorcunife" and 70/30 Cupro-Nickel, Copper, "Yorcalnic" (aluminium-bronze) and Tin Bronzes. They are also makers of Bi-metallic (Duplex) tubes and specialise in the manufacture of Heat Exchanger and Condenser Tubes. They are sole makers of "Yorkshire" Capillary Fittings.

"YORKSHIRE" BI-METALLIC** (Duplex) **TUBES

Bi-metallic or Duplex tubes are frequently used to overcome corrosion problems where no single alloy can provide adequate resistance to corrosion by the media in contact with the inside and outside surfaces of the tubes. "Yorkshire" Bi-metallic tubes are manufactured in combinations of steel and non-ferrous alloys, e.g. steel lined or shirted with "Yorcalbro", and in combinations of non-ferrous alloys.

"YORCALBRO"** (Aluminium-Brass) **TUBES FOR HEAT EXCHANGE EQUIPMENT

"Yorcalbro" has become a household word throughout the oil world and it can be relied upon to give satisfactory service in heat exchange equipment using sea or estuarine cooling water which is free from silt. Its main advantages are:

(1) High resistance to corrosion on both product and water side.
(2) Like other "Yorkshire" alloys, it is immune from attack by dezincification and season cracking.
(3) It renders possible the much longer "on stream" runs obtainable with refinery plant today.
(4) High water speeds are permissible with "Yorcalbro" tubes because of their resistance to corrosion-erosion, and initial heat transfer is better maintained with this alloy than with any other alloy.
(5) Although the cost of "Yorcalbro" is about 6 per cent higher than that of ordinary brass tubes, this is offset by its longer life and trouble-free service, resulting in reduced maintenance charges.

THE YORKSHIRE COPPER WORKS LTD · LEEDS & BARRHEAD

STRUCTURES IN STEEL

We Specialise in

ALL TYPES OF STRUCTURES

Required for

Oil Production and Refining

ALSO

'KELVIN' *all iron* and 'MAINSTEEL' PALISADING
and All Types of FENCING
for HOME and OVERSEAS

A. & J. MAIN & COMPANY LIMITED

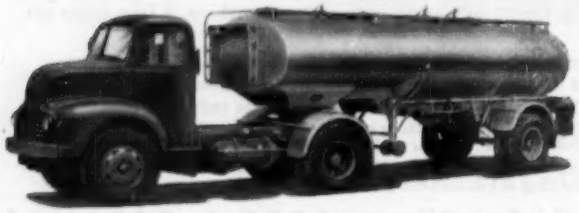
LONDON OFFICE
VINCENT HOUSE, VINCENT SQUARE, S.W.1
Telephones: Victoria 8375/6/7/8 *Telegrams:* Kelvin Sowest, London

WORKS AND REGISTERED OFFICE
CLYDESDALE IRONWORKS, POSSILPARK
GLASGOW, C.2
Telephone: Possil 8381 *Telegrams:* Kelvin, Glasgow

CALCUTTA: Post Box 36, 16 NETAJI SUBHAS ROAD
also NAIROBI and CHITTAGONG

'Expanded Compactness'

. . . sounds like a paradox but can fairly be applied to the modern Road Tank . . . the 'bulk' method of space-saving for payloads of Oils and Petroleum. Within the statutory weight limits all suitable items are now transported the bulk way, because of the obvious advantages of safe and speedy delivery, quick filling and discharge, and controlled temperature in transit.



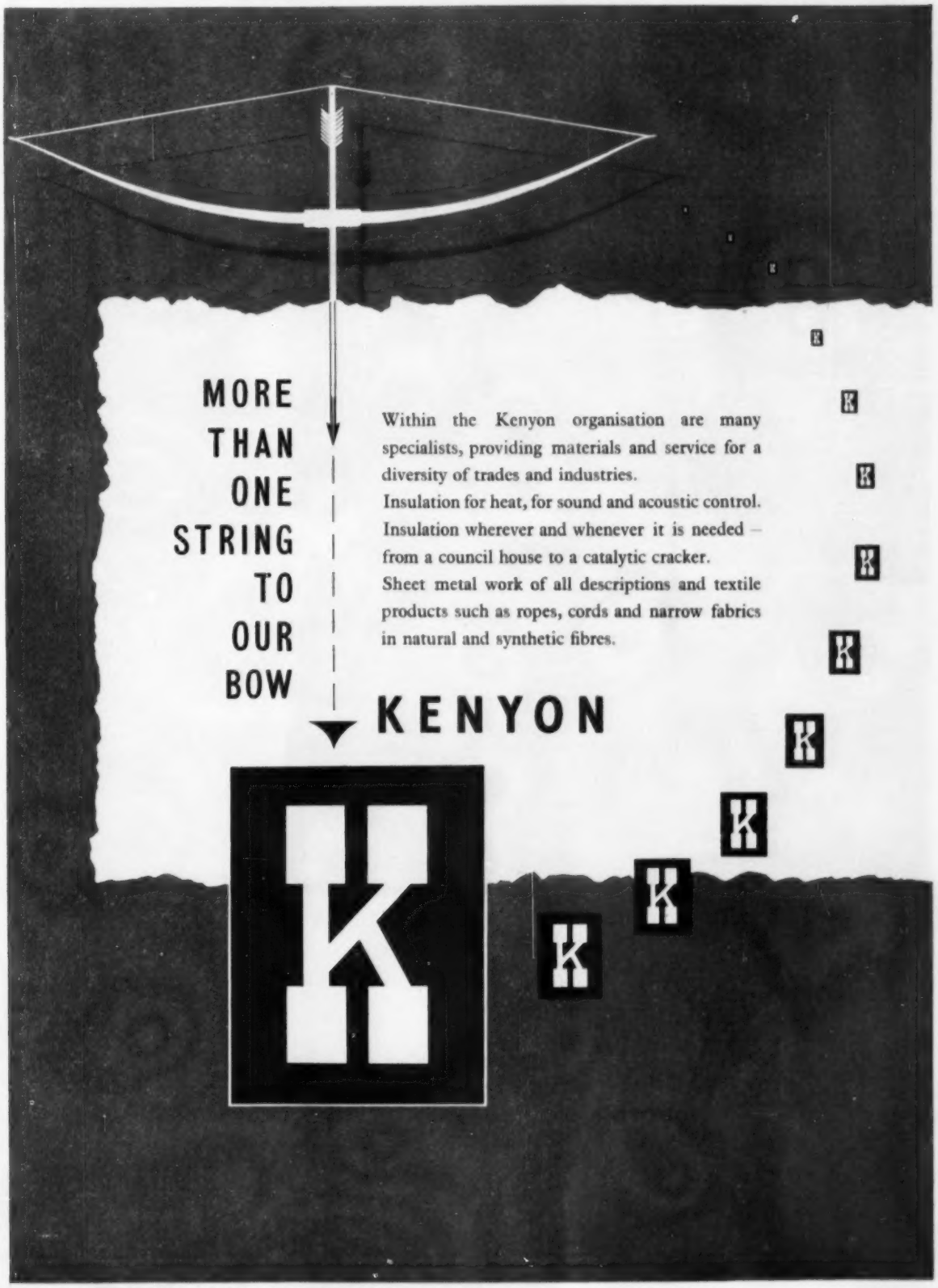
Butterfield Road Tanks are built to your specification with insulation as required. On the usual type of chassis, mounting is by the 'girder' principle, a Butterfield speciality which gives maximum support to the Tank and ensures great steadiness on the road. Tanks for mounting on articulated vehicles are often now 'stepped' to clear the trailer mechanism, thus preserving a straight and modern line.

girder mounting ensures stability

Butterfield ROAD TANKS

STAINLESS STEEL · MILD STEEL · ALUMINIUM

W P Butterfield Limited P.O. Box 38 Shipley Yorkshire Tel 52244 (8 lines)


MORE THAN ONE STRING TO OUR BOW
Within the Kenyon organisation are many specialists, providing materials and service for a diversity of trades and industries.
Insulation for heat, for sound and acoustic control.
Insulation wherever and whenever it is needed – from a council house to a catalytic cracker.
Sheet metal work of all descriptions and textile products such as ropes, cords and narrow fabrics in natural and synthetic fibres.
KENYON
WILLIAM KENYON & SONS LIMITED · DUKINFIELD · CHESHIRE
KH184

Destination

Kwinana

For the new Kwinana Refinery, tubes and tube plates for condensers and heat exchangers have been supplied by the Metals Division of I.C.I.

All the non-ferrous tubes for the platforming unit heat exchangers made by A. F. Craig & Co. Ltd., Paisley, were of I.C.I. 'Kunifer' 30 and Admiralty Brass.

I.C.I. CONDENSER TUBES AND PLATES

IMPERIAL CHEMICAL INDUSTRIES LIMITED, LONDON, S.W.1.

M385